Pattern formation by capillary instabilities in thin films
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Chapter 7

Capillary Instabilities in a Polymer Blend Film Driven by Surface Tension Gradients

7.1 Introduction

The influences of surface tension gradients on the hydrodynamics and mass transfer in fluid systems are often termed as the “Marangoni Effect”. Thin liquid films, are easily deformed by material heterogeneities and thermal fluctuations. Because these perturbations influence the long term stability and the qualitative structure of the film, a better understanding of these effects is required. The study of the surface–tension–gradient induced flow is pertinent to various applications where interfacial flows are encountered, such as in lubrication and coating processes. Moreover, surface–tension–driven flow is an interesting and important fundamental problem of fluid dynamics.

The physical basis for the deformation of a liquid surface by surface tension
gradients was first developed by Gibbs \cite{1}. Heat or mass transfer in liquids are nonequilibrium phenomena, often giving rise to instabilities, which lead to the formation of dissipative structures \cite{2, 3}. This type of instabilities was investigated in many papers and monographs \cite{4} especially at the liquid surface where these instabilities manifest themselves as a flow induced by surface tension gradients. An important precondition for the occurrence of such unstable modes is the existence of heat or mass transfer in the liquid layer, which results in temperature or concentration gradients in the region close to its surface. In this case, a surface tension gradient can arise due to this temperature or concentration dependence. The liquid layer becomes unstable due to normal \cite{5, 6} as well as lateral \cite{7, 8, 9} flows and gradients.

In thin films made of polymer blends, lateral phase separation often results in composition–dependent surface morphologies \cite{10}. When a polymer blend is in one phase region close to its critical temperature, composition fluctuations are significant. In addition, thermally–excited surface undulations affect the...
morphology of thin polymer films (see Chapter 5 of this thesis). In our case, composition fluctuations that give rise to surface tension gradients ($\Delta \sigma$), are mainly due to the mass transfer from the bulk to the film surface. Due to the small film thicknesses, temperature gradients across the film and surface elasticity influence on the surface tension can be ignored.

To study surface instabilities of polymer blend films, mixtures of polystyrene (PS) and poly(vinyl methyl ether) PVME were deposited onto chemically homogeneous silicon wafers. PS/PVME blends are known to be homogeneous at room temperature but to demix at higher temperatures, exhibiting a lower critical solution temperature (LCST). Kim et al. [11] found that the critical composition of the blend exhibits concentration fluctuations in the homogeneous regime close to the LCST. The extent of these fluctuations is inversely proportional to the absolute value of the temperature coefficient $B$ in the Flory interaction parameter

$$\chi = A + \frac{B}{T}$$

Several authors have studied the properties of the polymer/air interface of miscible PS/PVME blends. The parameters considered were blend composition, molecular weights and temperature. They demonstrated that PVME is enriched at the free surface, exhibiting a strong surfactant behavior that reduces the surface tension. Schmidt–Rohr et al. reported that on the scale of polymer segments, the PS/PVME blends are not completely mixed. The blend is neither homogeneous nor strictly phase separated but nano–heterogeneous. This was shown experimentally by performing a two–dimensional NMR spectroscopic study. Shimizu et al. investigated these domains for high molecular weight PS ($M_n \sim 50\text{Kg/mol}$). Their experiments indicated that the blend structure has a percolation–like morphology similar to typical structures observed in spinodal decomposition. Additionally, they demonstrated that the domain size depends strongly on the molecular weight of the blend components.

This chapter focuses on a new type of instability that develops spontaneously in a PS/PVME polymer blend film. From an experimentally point of view, we observed the instability and measured its wavelength versus film thickness and blend composition. Furthermore, we were able to direct and manipulate the instability in a lithographic process.
Table 7.1: *Critical and annealing temperatures of different blend compositions.*

<table>
<thead>
<tr>
<th>Blend composition</th>
<th>$T_d$ $^\circ\text{C}$</th>
<th>$T_g$ $^\circ\text{C}$</th>
<th>$T_w$ $^\circ\text{C}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%PS – 90%PVME</td>
<td>45 ± 2</td>
<td>-28.53</td>
<td>35</td>
</tr>
<tr>
<td>20%PS – 80%PVME</td>
<td>40 ± 1.5</td>
<td>-23.39</td>
<td>28</td>
</tr>
<tr>
<td>40%PS – 60%PVME</td>
<td>45 ± 2</td>
<td>-10</td>
<td>30</td>
</tr>
<tr>
<td>50%PS – 50%PVME</td>
<td>50 ± 2.5</td>
<td>-2.24</td>
<td>35</td>
</tr>
<tr>
<td>60%PS – 40%PVME</td>
<td>55 ± 2</td>
<td>4</td>
<td>40</td>
</tr>
<tr>
<td>80%PS – 20%PVME</td>
<td>70 ± 2.5</td>
<td>13.41</td>
<td>65</td>
</tr>
</tbody>
</table>

$T_d$ Demixing temperature.

$T_g$ Glass transition temperature of the blend.

$T_w$ Working temperature.

### 7.2 Experimental Section

A schematic description of our experimental setup is shown in Fig.(7.1c). PS ($M_w = 32 \text{ kg/mol}$, polydispersity $M_w/M_n = 1.02$) and PVME ($M_w = 52 \text{ kg/mol}$, $M_w/M_n = 1.04$) were used as received. Films of mixtures with volume fractions $\varphi$ ranging from $\varphi_{PVME} = 0.2$ to $\varphi_{PVME} = 0.8$ were spin–coated from a toluene solution onto silicon wafers. Prior to deposition, the substrates were cleaned in a jet of CO$_2$ crystals (“snow–jet”). Subsequently, the substrates were immersed in a hot ($\sim 80^\circ \text{C}$) Piranha solution$^\text{[1]}$. The samples were annealed at $T - T_g(\varphi) = \text{const.}$, the condition of constant chain mobility. The annealing temperatures were below the binodal curve of the blend to prevent the demixing of the two components. Their values are given in Table 7.1 together with the demixing ($T_d$) and glass transition temperatures ($T_g$) of the blends for the range of compositions used in this study.

Our blend exhibited a lower critical solution temperature of $40^\circ \text{C}$ at a

$^\text{[1]}$ The “Piranha” solution consists of a mixture of hydrogen peroxide and sulphuric acid in a ratio of 1/3 w/w.
critical composition of $\varphi_{\text{PVME}} = 0.8$. The experiments were performed in a glove box with a water vapor concentration of less than 1 ppm. This was necessary because PVME is highly hygroscopic. Thin films with thicknesses ranging between 60 nm and 310 nm were prepared by spin coating. The sample morphology was followed during heating using a Mitutoyo WF reflection microscope and the images were recorded with a Carl–Zeiss digital camera. A DI Dimension 3100 AFM was used in tapping mode to acquire topographic and phase micrographs after cooling the sample to room temperature.

We studied the film instability when the blend was in a mixed state, bellow
Figure 7.3: Wavelength vs. film thickness for four blend compositions.

its critical temperature. Because the blend was above its glass transition temperature \(T_g\), its composition fluctuates with time. These fluctuations occur in the bulk as well as at the surface. In the bulk, the fluctuations relax by diffusion while at the surface, they induce surface tension gradients. Short wavelength composition fluctuations are unlikely to destabilize the free interface because they can easily decay by diffusion processes. On the other hand, long wavelength fluctuations build up surface stresses causing flow of bulk material towards regions of high surface tension. If the hydrodynamic response is faster than diffusion, a capillary instability sets–in and breaks–up the thin polymer film.

First, the influence of the film thickness on the morphology of the blend was studied, keeping the composition of the mixture constant. In Fig.7.2, the
Figure 7.4: Optical micrographs (50 × 50 µm²) showing unstable morphologies of a ~130 nm thick polymer film for different composition of the polymer blend (a) 60PS/40PVME; (b) 50PS/50PVME; (c) 40PS/60PVME; (d) 20PS/80PVME.

Topography of a 40%PS–60%PVME blend is shown as a function of film thickness. The optical images show the spontaneous deformation of the polymer–air interface upon annealing the samples at 30°C. Morphologies similar to those in Fig. 7.2 were observed for the range of blend compositions given in Table 7.1. The wavelength of the instability (λ) was determined by Fourier transformations of such images and plotted versus film thickness (Fig. 7.3). These measurements show that the wavelength increases with increasing the film thickness. Because all the samples were annealed for the same time, an increase in λ due to coarsening is unlikely.

The results may be explained in terms of hydrodynamic arguments. The
most amplified wavelength is determined by the coupling between the composition fluctuations and the rheological behavior of the polymer blend. The surface tension gradients caused by composition fluctuations should be independent by the film thickness for all films of identical blend composition. Therefore, we assume that only the rheological behavior influences the wavelength of destabilization. Short wavelength instabilities are strongly damped by the surface tension, while building–up long wavelength oscillations is opposed by the viscous drag of the hydrodynamic flow. Therefore, the characteristic wavelength is dictated by the interplay between the surface tension and the energy dissipation in the polymer film. For thinner films the viscous drag is higher in comparison to thicker films when assuming a non–slip Poiseuille type of flow inside the layer (Fig. 7.1c). Therefore, smaller wavelengths are favored. For thicker films, the hydrodynamic drag decreases and therefore the instability wavelength increases.

In a second class of experiments, we analyzed the influence of the blend composition on the surface morphology. We measured the instability wave-
length for four different compositions (40–60, 50–50, 60–40 and 80–20 PVME–PS), keeping the film thickness constant (∼130 nm). The results are shown in Fig.(7.4).

Analyzing the data from Fig.(7.4), we observed that the wavelength shows a minimum for the symmetric composition 50%PS–50%PVME (Fig. 7.5). Shifting the composition either to smaller or larger volume fractions of PVME resulted in an increase in λ.

This effect may be explained in terms of composition fluctuation arguments. The volume fraction of the PVME varies from ϕ_s at surface to ϕ_∞ in the bulk (Fig. 7.1a). Furthermore, the composition fluctuations at the surface induce lateral variations in the surface tension (Fig. 7.1b) which depend by the volume fraction of the PVME at the surface and in the bulk. The largest surface tension gradients are expected for a symmetric mixture, because of the strongest enrichment of PVME at the interface. For other compositions, the enrichment is lower, resulting in weaker lateral surface tension gradients. A smaller gradient implies a weaker stress at the film surface, therefore, larger instability wavelengths. The behavior described above is summarized in Fig.(7.5), where the instability wavelength is plotted versus the volume fraction of PVME.

Theoretically, film instabilities are usually computed by a linear stability analysis. We present here a possible route to compute the instability wavelength. Most film instabilities reported so far, have been predicted essentially by this method. Examples include the Mullins–Sekerka instability in solidification [12], the Saffman–Taylor instability in the viscous fingering problem [13] and the convective Bénard instability [14]. Even though all these instabilities give rise to complex patterns, they are all triggered by infinitesimal perturbations [15]. We refer to these as linear instabilities because they can be explained by a linear analysis. In our case we postulate a coupling of the composition fluctuations with the material flow. To model the system, the Navier–Stokes equation describing the rheological behavior of the system must be used, while a Cahn–Hilliard type equation [16, 17] describes the composition fluctuations in the polymer blend. By solving the resulting system of partial differential equations, the most probable mode has to be computed. However, the solution is impossible to be computed analytically. Due to its great complexity, the system of coupled partial differential equations can be solved only numerically. We are currently performing these calculations, their
Figure 7.6: Onset of film instabilities of a 110 nm thick PS/ PVME film that was heated to 170°C for 60 s, (a): confined between two silicon wafers spaced at \( d = 308 \) nm; (b) no confinement. The undulatory character of the structures is due to a spontaneous surface instability in both cases. The larger amplitude of the surface undulation in (a) indicates an earlier onset of the instability compared to (b), presumably due to differing initial heating rates when placing the sample in the oven. This accounts also for the more coarse grained appearance of the structure in (a) due to a longer coalescence time.

result being the subject of a future publication

### 7.3 Surface Tension Driven Lithography

By understanding the destabilization process, we were able to harness and use the instabilities in a pattern-replication process. The lithography using electric fields and temperature gradients is robust and versatile but the external interaction with the structure formation process may be a limitation. This disadvantage can be circumvented by making use of film instabilities that are intrinsic to the system. If confined by a topographically structured surface, any undulatory mode of a film instability can be harnessed to induce structure into the film.

A liquid film has a peculiar behavior in a confined environment. Its morphology in the capillary regime is dominated by a minimization of the overall surface free energy. This regime is defined by a characteristic parameter, the
so-called capillary length \( a \)

\[
a = \sqrt{\frac{2 \gamma}{\rho g}} \tag{7.1}
\]

quantifying the balance between the surface energy \( \gamma \) and the gravitational acceleration \( g \). In Eqn. (7.1), \( \rho \) is the density of the liquid. On a flat, solid surface that is smooth and chemically homogeneous, the shape of the liquid is dictated by the balance of the liquid–vapor, liquid–substrate and substrate–vapor surface free energies [18]. In case of a liquified polymer, the vapor pressure is zero. When the interface between the liquid and a confining solid has a lower energy per unit area compared to the liquid–air and the solid–air surfaces, this leads to liquid morphologies that are not observed for large volumes of liquids. Examples include the capillary rise of a liquid in a narrow tube, the formation a liquid bridge spanning two opposing finger tips, or the fact that large amounts of water are drawn into a granular material (e.g. sand), overcoming the gravitational counterforce.

In the first part of this chapter, we showed that a liquid polymer blend becomes spontaneously unstable due to surface tension gradients. Coupling the effect of capillarity with liquid instabilities (Fig. 7.7) in a confined geometry, the liquid forms capillary bridges. Quenching the liquid polymer film to temperatures below its solidification temperature, the structures can be frozen for further analysis.

7.3.1 The Experimental Situation. Results and Discussions.

The following work was performed by Harkema et al. [19] and is presented here for the sake of completion. Spontaneous surface instabilities in thin PS/PVME polymer blend films were used to create surface patterns. The unstable film was observed in two conditions (Fig. 7.6): in the presence and in the absence of a confinement. Fig. (7.6a) shows an unstable 110 nm thick PS/ PVME film heated to 170°C, (a) confined to a 308 nm wide slit and (b) in the absence of confinement. The film instability was explained in Section 7.2.

The behavior of the liquid polymer in a confined geometry is schematically depicted in Fig. (7.7). Depending by the initial film thickness \( h \) and by the maximal confinement \( d \) (i.e. the lowest value of the inter–plate spacing) the final structures of the polymer film can be divided into three regimes [19]. This section focuses only on the case when \( d \gtrsim h \) (Fig. 7.7e).
For $d \lesssim h$, the initial undulations of the film (Fig. 7.7a) lead to a bridging of the liquid between the two plates (Fig. 7.7c). If the confining plate is patterned (Fig. 7.7d), these bridges form in the regions of greatest confinement, i.e. at the locations where the topographic pattern of the top plate extends down towards the polymer film.

In Fig. (7.8), the replication of a line pattern is shown. The 24 lines of the master are replicated by the formation of capillary bridges – the polymer spans from the substrate to the confining surface. The obtained structure (Fig. 7.8b) is a positive replica of the master (Fig. 7.8a).

A second replicated structure is shown in the AFM images of Fig. (7.9). They correspond to the replicated polymer pattern (Fig. 7.9d) and the confining plate (Fig. 7.9e). The two micrographs clearly show the nature of the replication process as opposed to the cases of imprinting and replication by capillary filling [19], which produce a negative replica of the master electrode. The positive replication of the hexagon-shaped holes on a triangular lattice clearly shows the novel nature of the replication process.

Replication occurs for two conditions.
Figure 7.8: The dewetting in a confined geometry. The 24 replicated lines in a) correspond to the 24 downward protruding lines of the master schematically shown in part a). These lines were replicated into the polymer film by capillary bridging \( d/h = 1.4, h = 84 \text{ nm} \).

- for capillary bridging to take place in a more or less homogeneous fashion, there has to be an approximate matching of the instability wavelength \( \lambda \) and the periodicity of the confining pattern

- per unit area \( A_0 \), the volume of the initial film must be laterally accommodated in the replicated structure.

The second condition can be written as

\[
\frac{d}{h} \approx \frac{A_0}{A_p}, \tag{7.2}
\]

where \( A_p \) is the lateral area of the protrusions of the confining surface extending down towards the polymer film (Fig. 7.7c). The first condition has to be fulfilled within an order of magnitude, but also the second condition allows some variation, since a certain degree of lateral under- or overfilling of the pattern is permissible.

To successfully replicate the master pattern, its surface has to be apolar. Highly apolar surfaces are typically not wetted by any liquid, since the coating of the surface by the liquid does not reduce its effective surface energy. In Fig. (7.8) and (7.9), capillary forces that drive the polymeric liquid to completely fill the surface pattern are absent. This enables the formation of the metastable morphologies corresponding to Fig. (7.7c).
7.4 Conclusions

In summary, our observations indicate a coupling of the composition fluctuations to the rheological behavior of the polymer film. The two effects strongly influence the resulting morphology. Stresses at the interface generated by composition fluctuations induced surface tension gradients, give rise to a capillary instability. The liquid film responds to these stresses by moving material towards regions of high surface tension. Therefore, the film buckles at a well defined wave number. Eventually, the process causes complete dewetting of the film from the substrate.

In a confined geometry, by suitably choosing the experimental parameters, the undulatory mode of the PS/PVME blend can used to produce positive replicas of a master pattern. While the well-known embossing and capillary filling techniques result in a negative replica of a surface pattern, a novel phenomenon was observed for a confinement with \( d \gtrsim h \). In this case, metastable liquid morphologies are formed by the interplay of dewetting and capillary bridging. This lithographic method can prove useful when external interactions with the polymeric material have to be avoided. For example, by using the process of dewetting in a confined geometry, an electrically active polymer
film can be patterned without the use of an external electric field that could damage the polymer.
Chapter 7. Film Instabilities by Surface Tension Gradients
Bibliography


