Solvent evaporation of spin cast films:
"crust" effects

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Abstract

When a glassy polymer film is formed by evaporation, the region near the free surface is polymer rich and becomes glassy first, as noticed long ago by Scriven et al. We discuss the thickness of this "crust" and the time interval where it is present -before freezing of the whole film. We argue that the crust is under mechanical tension, and should form some cracks. This may be the source of the roughness observed on the final, dry films, when the solvent vapor pressure is high (and leads to thin crusts).

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Shortened version of the title:

SPIN CAST FILMS

1 Introduction

Spin cast polymer films are used in many industrial sectors (electronics, packaging, ...). But the birth of the films is complex: during the (rapid) solvent evaporation, many things happen. In particular, one can think of:

a) thermal (Rayleigh Benard) instabilities (since the free surface is cooled down).

b) convective instabilities due to concentration effects (when the surface tension of the polymer $\gamma_p$ is higher than the surface tension of the solvent $\gamma_s$): a solvent rich plume lowers the surface tension, and this enhances the plume.

We recently argued [1] that (when $\gamma_p > \gamma_s$) process (b) should dominate over process (a).

In the present note, we are concerned with another phenomenon. Strawhecker et al [2] found that the surface roughness of the final films is anomalously high ($\sim 50 \text{nm}$) when the pure solvent has a high vapor pressure.

This cannot be explained by process (b) above: a number of polymer solvent pairs with $\gamma_p > \gamma_s$, give a smooth surface (e.g. PS/toluene on PVME/water). Also, some systems with $\gamma_p < \gamma_s$, give a rough surface (e.g. PS/acetone or PVME/methanol).
This led us to another line of thought, based on the glassy nature of the final state: a polymer rich "crust" builds up near the free surface: when it dries out, it is under tension and it should rupture -creating a rough surface.

In section 2, we discuss the concentration profiles in the film, and the formation of the crust. This has been analysed many years ago in precise numerical calculations by Bornside, Macosko and Scriven [3]. Here we set up a much cruder, but more transparent, model. In section 3, we produce a crude estimate of the mechanical tensions, and discuss the possible forms of rupture. All our analysis is qualitative: any improvement on this would require a deep (non existent) knowledge of the glass transition induced by solvent depletion.

2 Crust formation

2.1 Transport in air

The aspect of the concentration profiles at one, given instant $t$ during evaporation is shown on fig. 1. The solvent volume fraction $\psi$ has a high value $\psi_d(t)$ at the bottom plate, and a low value $\psi_u(t)$ at the free surface. Immediately above this, we have $\psi = \psi_g$. This value corresponds to a solvent partial pressure $p_g$ in the neighboring gas. Inside the gas, we assume a diffusion layer of fixed thickness $\ell$: this is a crude approximation to the actual boundary layers which are associated with air motions in the laboratory.

Figure 1: solvent volume fractions near the first freezing time ($t = t^*$) (qualitative picture)

The outward solvent current (in air) is related to a diffusion coefficient $D_{\text{air}}$:

$$J = D_{\text{air}} \frac{p_v}{kT} \ell$$

(1)

Here, $p_v/kT \equiv \varphi_g/a^3$ is the number density of solvent just above the interface, and $J$ is a number of molecules per unit area and unit time. The diffusion constant $D_{\text{air}}$ is of order $v_{\text{th}}\lambda$, where $v_{\text{th}} = (kT/m)^{1/2}$ is the thermal velocity for solvent molecules of mass $m$, and $\lambda$ the mean free path in air (inversely proportional to the atmospheric pressure $p_a$). This gives ultimately:
\[ D_{\text{air}} \sim \frac{\nu_{\text{th}} kT}{a^2 p_a} \]  

(2)

where \( a \) is the size of a solvent molecule.

We are thus led to an evaporation current:

\[ J = \frac{\nu_{\text{th}} p_g}{a^2 \ell p_a} \]  

(3)

2.2 Local equilibrium at the free surface

We assume, for simplicity, that the volume fractions just below \((\psi_u)\) and just above \((\psi_g)\) the interface are related by Henry’s law, with a constant coefficient:

\[ a^3 \psi_g = \frac{p_g}{kT} = \psi_u \frac{p_v(T)}{kT} \]  

(4)

where \( p_v \) is the vapor pressure of pure solvent. This assumption ignores many delicacies in the sorption desorption curves \([3], [5]\), but it should be sufficient for our purposes. Eqs (3, 4) then give us:

\[ J = \frac{a^3 \psi_u}{a^3} = \frac{\nu_{\text{th}} a p_v(T)}{\ell p_a} \psi_u \]  

(5)

(where \( a^3 \) is the volume per solvent molecule in the liquid solvent).

2.3 Steady state currents in the crust region

Inside the crust, we assume that a steady state is achieved, with the same current \( J \). If we call \( D(\phi) \) the diffusion coefficient of the solvent in the mixture, we may write:

\[ J = D(\phi) \frac{d\phi}{dx} \]  

(6)

The coefficient \( D(\psi) \) varies with \( \psi \) for two reasons:

a) the mesh size \( \xi \) of the polymer solution increases with \( \psi \);  
b) at low \( \psi \) the system is glassy and \( D(\psi) \) becomes very small.

Effect (a) is minor compared with effect (b), and we shall omit it in the following. To get a practical feeling about \( D(\psi) \) in the small \( \psi \) region, it is helpful to use a free volume picture for the glass transition \([6]\). The free volume parameter \( v \) has one component \( v_1 \) present in pure polymer and another component proportional to the volume fraction of solvent:

\[ \frac{v(T_1 \phi)}{a^3} = \frac{v_1(T)}{a^3} + k\psi \]  

(7)

(where \( k \) is a coefficient of order unity).
We shall focus our attention on the region where solvent effects dominate over temperature effects ($\psi > \psi_1 / a^3$). This then gives:

$$D(\psi) = D_1 \exp \left( \frac{q}{\psi} \right)$$

where $q$ is another coefficient of order unity, and $D_1$ is the diffusion constant in a very fluid mixture ($\psi \sim 1$). Where we know an explicit form of $D(\psi)$ such as eq. (8), we can find the steady state profile in the crust region by integrating eq. (7) over, as thickness $x$ near the free surface:

$$x = J \int_{\psi_u}^{\psi} D(\psi') d\psi'$$

Eq. (9) holds only in the region of small $D$, which acts as a barrier, when the assumption $\partial J / \partial x = 0$ is valid. Outside of the barrier, diffusion is fast and the profile $\psi(x)$ is nearly flat.

Note that the presence of a crust, as it is understood here, is independent of the presence (or absence) of an adsorbed polymer layer near the free surface. An adsorbed layer will be present if $\gamma_p < \gamma_s$, and if the adsorption time is shorter than the overall time for spin casting. But this layer is expected to be very thin; the number $\Gamma$ of adsorbed monomers per unit area should be $\Gamma \sim a^{-2}$: a thin layer like this cannot be really glassy, and does not contribute significantly to the crust.

### 2.4 The crust thickness

We can now define the thickness of the crust $b$ via the initial slope at $x = 0$ (the free surface):

$$\frac{1}{b} = \frac{1}{\psi_u} \frac{d\psi}{dx} \bigg|_{x=0}$$

Using eqs (5, 6), this gives:

$$b = \ell \frac{p_n D(\psi_u)}{p_v v_{th} a}$$

The solvent fracture $\psi_u(t)$ decreases with time: at a certain instant $t^*$, it reaches a critical value $\phi^*$ below which the polymer solvent system is glassy. The central parameter is the crust thickness $b^*$ at this moment:

$$b^* = \ell \frac{p_n D(\psi^*)}{p_v v_{th} a}$$

For instance, let us use the general form (8) for $D(\psi)$, with $q = 1$ and $\psi^* = 0.2$. Taking $\ell = 1mm$, $p_n/p_v = 10$, and $D_0/av_{th} = 10^{-3}$, we arrive at $b^* = 70$ nanometers. Thus the crust is indeed thin for practical conditions.

Another important feature of eq. (12), is the dependence on the vapor pressure $p_v(T)$: large vapor pressures lead to thin crusts. This, in turn, implies that the crust will be more fragile, as discussed in section 3.
2.5 Lifetime of the crust

The birth of the crust occurs at a certain time \( t^* \) (when \( \psi_u = \psi^* \)). At a later time \( t^{**} \), the whole film becomes glassy (when \( \psi_d = \psi^* \)). We shall now assume that \( t^{**} - t^* \) is (like \( t^* \)), proportional to the overall evaporation time \( \tau_{ev} \). A simplified discussion of \( \tau_{ev} \) is given below.

We concentrate on regimes where \( b \) is smaller than the overall thickness \( e(t) \). Then, the total amount of solvent in the film is \( Q \sim e \psi_d \) (per unit area of film).

The rate of change of \( Q \) is given by:

\[
\frac{dQ}{dt} = -\frac{J}{a^3} + \phi_u \frac{de}{dt} \tag{13}
\]

where the first term describes evaporation, while the second term is related to the presence of a moving boundary.

The conservation of polymer imposes:

\[
e - Q \equiv e(1 - \psi_d) = e_f \tag{14}
\]

where \( e_f \) is the final thickness of the dry film.

Eqs (13, 14) must still be supplemented by one relation relating \( \psi_d \) to \( \psi_u \).

We shall obtain this in a very crude fashion, by considering the cross over point between crust and "inside" the film. We assume that at \( \psi = c \psi_u \) (where \( c \) is a numerical coefficient of order 2), the diffusion coefficient \( D(\psi) \) has become fast: then the profile is flat, and this implies \( \psi = \psi_d \). Thus, we are led to the ansatz:

\[
\psi_d = c \psi_u \tag{15}
\]

Then the system (13-15) can be reduced to:

\[
ce d\psi_u + de(c - 1)\psi_u = -\frac{J}{a^3} dt = -A \psi_u dt \tag{16}
\]

with:

\[
A = \frac{\nu_{th} a p_a}{\ell \, p_v} \tag{17}
\]

Eq. (16) together with eq. (14) can be integrated in detail. But, for our purposes, it is enough to note that it involves a single time constant \( \tau \):

\[
\tau_{ev} = c^{-1} \frac{e_f}{A} \tag{18}
\]

In the form (13), \( \tau \) is exactly the relaxation time in the final stage, where \( e \to e_f \) and \( de/dt \) can be neglected.

Thus, we are led to postulate that the duration of the crust regime follows the scaling rule:

\[
t^{**} - t^* \sim \tau_{ev} \sim \frac{e_f}{A} \sim \frac{e_f \ell}{\nu_{th} a \, p_v} \tag{19}
\]
3 Rupture of the crust and resulting effects

We now focus our attention on the interval \( t^* < t < t^{**} \), where the crust is present over a sheet of fluid solution. During this interval, the volume fraction \( \psi_u(t) \) at the free surface decreases from \( \psi^* \) down to a finite fraction of \( \psi^*/c \): this would ensure that the volume fraction at the bottom plate \( \psi_d \) reaches the threshold \( \psi_d(t^{**}) : \psi^* \) at the end of the interval.

Following the ideas of Leibler and Sekimoto [5], we believe that a network is formed in the crust as soon as \( \psi_u(t) \) reaches \( \psi^* \). At later times, this network is deswollen (as explained on fig. 2), because \( \psi \) decreases down to \( \psi^*/c \). The volume of the gel decreases, but its horizontal dimensions have to remain the same. Thus, there is a tensile stress in the crust.

Figure 2: the "crust": a) overall view b) enlarged view of one mesh unit at the first freezing time \( (t = t^*) \) c) the same unit, at later times \( (t \sim t^{**}) \), is under horizontal tension.

The overall contraction ratio is of order:

\[
\theta = -\psi_u(t^{**}) + \psi_u(t^*) \cong \psi^* \left( 1 - \frac{1}{c} \right) \cong \psi^* \tag{20}
\]

and the tensile shears stress \( \sigma \) is predicted to be:

\[
\sigma \cong \Pi(\psi^{**})\theta = \Pi(\psi^{**})\psi^* \tag{21}
\]

where we have replaced the elastic modulus of the gel by the osmotic pressure of the polymer \( \Pi \), which scales in the same way. Because at \( \psi = \psi^{**} \) we are dealing with rather concentrated solutions, we may write simply [4]:
The ratio of stress to elastic modulus is thus expected to rise up to a value:

\[
\frac{\sigma}{\Pi(\psi^{**})} \sim \psi^*
\]  

(23)

With the usual values of \(\psi^* (0,2)\), this should be sufficient to induce fracture in the crust. Fracture is indeed favored because a) the crust is thin b) it must have the usual syneresis, leading to rather open regions which can play the role of a nucleation center.

Thus, we are led to suggest that the outer surface of the film exhibits a network of fracture lines at times \(t < t^{**}\), very much like earth at the bottom of a drying pond. The evaporation flows should then converge towards these fracture lines, and a rough interface should appear. We are not able to predict the density of cracks, nor the amplitude of the resultant roughness. But it is clear that this process should be important, mainly when the crust is thin. By eq. \(\text{(12)}\) this requires a high vapor pressure \(p_v\) for the solvent -in agreement with the results of ref. \(\text{[2]}\).

How could we test these ideas?

\textbf{a}) apart from acting on \(p_v\), we could also possibly act on the boundary layer conditions (described by \(\ell\) in eq. \(\text{(12)}\), or decrease the air pressure.

\textbf{b}) some direct observation may be possible. Crusts have been observed in deswelling experiments by Tanaka and coworkers \(\text{[8]}\), using optical microscopes. They did see crust rupture after some deswelling. In the present case, it may be better to probe the surface (after complete drying) with an AFM tip.

Cracks are the most plausible channel for relaxation of the tension. But the following evaporation flow may lead to other forms -e.g. "volcanic" landscapes.

To summarize: all our discussion is extremely qualitative, and it may be insufficient at some points. However, we believe that a) the compact formula \(\text{(12)}\) for the crust thickness may be useful b) crust rupture is indeed a plausible explanation for the surface roughness of the films.

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