A Universal Nucleation Mechanism for Solvent Cast Polymer Film Rupture

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It is shown that the intrinsic stress in solvent cast polymer coatings plays a key role in the nucleation of holes in the film. Nucleation is important because it is meanwhile clear that heterogeneous nucleation is the only relevant rupture mechanism for the technologically relevant thickness regime well above 100 nm. The most striking feature is that in contrast to what has been widely believed, the number density of holes scales not algebraically, but exponentially with the film thickness.

If one deposits a thin liquid film on a solid substrate, such as a freshly prepared laquer coating, one usually wishes it to stay homogeneously in place. However, if the equilibrium contact angle of the film material is finite, the film can gain free energy by beading off the substrate and forming an array of individual droplets. In order to avoid this dewetting process, a thorough understanding of the basic mechanisms is necessary.

For films thinner than about 100 nanometer, the initial formation of dry spots may proceed via three distinctly different mechanisms. Dry patches may nucleate at impurities or inhomogeneities (heterogeneous nucleation), or by thermally excited indentations in the free film surface (thermal nucleation). Furthermore, capillary waves on the film may be unstable and grow in amplitude until their troughs reach the substrate, where they form dry spots (spinodal dewetting). The interplay of these dewetting modes has only recently come close to a complete understanding.

For the technologically much more relevant thickness regime well above 100 nm, it is meanwhile clear that heterogeneous nucleation is the only relevant mechanism for the overwhelming majority of systems. In this scenario, a random array of circular holes form immediately, one at each nucleation site. They grow in time until all of the film has been removed. If the nucleation centers could be completely removed from the film, the latter would be metastable, and usually last sufficiently long for most applications. It is therefore of particular importance to investigate the very nature of the nucleation centers. Since the most relevant material class in this context are polymers deposited from solution, we used solvent cast polystyrene films on silicon wafers as a model system, and we restrict our discussion to this frequently encountered type of film throughout this paper.

The most obvious project is to try to reduce the number of nucleating holes by cleaning up the film material and the preparation conditions. However, the amazing gap observed between enormous cleaning efforts on the one hand, and the poor success on the other, suggests that the physics of hole nucleation in polymer films may be deeper than a mere effect of ‘dirt’. We have thus investigated the possible interplay between the nucleation of holes in the film, and some possible strain in the material induced by the preparation procedure.

In fact, it is well known that solvent cast polymer films are considerably strained by means of a quite fundamental mechanism: as the solvent evaporates and the film becomes thinner, the glass transition temperature, \( T_g \), of the solution gradually increases from well below room temperature to the glass transition temperature of the pure polymer, which is about \( T_g = 100^\circ \text{C} \) for polystyrene. As long as \( T_g \) is below room temperature, the polymer molecules are mobile and retain their equilibrium configuration, the gyration ellipsoids of the individual molecules averaging to a sphere. However, as \( T_g \) increases above room temperature, equilibration of the molecules is hindered, such that the (averaged) gyration ellipsoid is flattened as the film thins further. The strain generated in this way is thus determined by the solvent content of the film when \( T_g \) equals room temperature, and is largely independent of other parameters, such as the rate of evaporation, or the film thickness. For instance, the stress in a polystyrene film cast from toluene at about 20\(^\circ\) C is, quite universally, 14 MPa.

In order to investigate the dewetting behavior of polystyrene films with different strain but otherwise identical properties, we had to find a way to vary the strain in a controlled manner. Polystyrene films were thus spin cast from toluene solution onto mica substrates. Since polystyrene wets mica completely, the films could be annealed on the mica substrate without any formation of holes, and the annealing step should change the amount of stress in the film. Afterwards, the annealed films were floated onto millipore water and transferred to hydrophobized silicon wafers and heated above \( T_g \), such that dewetting could commence. The formation of holes was observed with an optical reflection microscope.

In Fig. 1 we show the number density of holes forming in a 60 nm thick film of 52 kg/mol polystyrene, as a function of the annealing time. Each data point corresponds to several prepared samples, the error bars represent standard deviations. Annealing was done at 140\(^\circ\)C, which is 40 degrees above the bulk glass transition \( T_g \) temperature. As one can clearly see, the number of holes decreases significantly with increasing annealing time. It is important to mention, though, that a reduction of hole density cannot be achieved by reducing the residual solvent content of the film, for instance by...
storing the samples under vacuum or by annealing them to a temperature below $T_g$. Only annealing above $T_g$ will result in a reduction. This shows that the mechanism of hole nucleation must be intimately connected to a material property of the film which is reduced upon annealing, such as the intrinsic strain. The solid line is an exponential fit to the data, indicating a decay time of $\tau_0 = (240 \pm 20) \text{s}$ Within our experimental scattering, the data are also consistent with a stretched exponential, $\exp(-t^{\beta})$, with $\beta$ between 0.8 and 1.1. However, since no significant deviation from a pure exponential is observed, the decay will henceforth be characterised by a single decay time, assuming $\beta = 1$.

It is clear from Fig. 1 that there is a residual subset of nucleation sites which is not removed by annealing. We will refer to the number density of these sites as $n_0$. However, a significant reduction of the number density of holes, as displayed in the figure, was invariably observed, and deserves thorough investigation. We thus repeated the procedure with films of 390 kg/mole polystyrene, and found a decay time of $\tau_0 = (510 \pm 200) \text{s}$. The ratio of the two decay times is close to the ratio of the self-diffusion constants determined by NMR for these molecular weights \footnote{R. Seemann, S. Herminghaus, and K. Jacobs, Phys. Rev. Lett. (2001) in print.}. This corroborates that microscopic changes in molecular configuration are probably responsible for the drastic changes in the number density of nucleation sites.

Let us now discuss the dependence of the number density $n_\ast$ of nucleation sites which are deactivated or removed by annealing. It corresponds to the difference of the initial number density of holes and the number density found after long annealing times. It is particularly rewarding to plot this quantity as a function of film thickness, $h$. This is done in Fig. 2, which shows the data along with a simple exponential fit. Good agreement is found, over a range of five orders of magnitude in number density. This suggests a fundamental law behind the nucleation of holes, and calls for explanation by a theoretical model.

What may be the microscopic nature of defects causing a local reduction in strain? A straightforward model is to assume these to be defects in the entanglement of the polymer chains. Regions of (accidentally) reduced entanglement will always be present, as a matter of mere statistics, and the material will be ‘weaker’ there. But how can an object as gentle as an entanglement defect induce an indentation going all the way through the film and finally reaching the substrate, forming a dry patch? It very probably won’t! Instead, quite a number of such defects must be present within the size of a typical indentation, in order to create an indentation deep enough to reach the substrate and initiate dewetting. If the density of these defects is constant within the polymer, as it is to be assumed, the probability of a certain number of defects being accumulated within the size of an indentation, which is the condition of forming a hole, decays exponentially with the film thickness. This is a quite robust result, and within our model explains the exponential law displayed in Fig. 2.

As a final test of the ideas presented here, let us discuss what we would expect for the dependence of the density of holes as a function of molecular weight. As the latter is reduced below the limit of entanglement, the defects must vanish. Consequently, we expect, roughly and qualitatively, that the number of holes increases with increasing molecular weight. In Fig. 3 we have plotted the density of holes in films of 60 nm thickness for variable molecular weight. The increasing tendency is clearly corroborated. An investigation of the fact that the data are consistent with a linear relationship, however, goes beyond the scope of this paper, and must be left to further studies.

In conclusion, we have obtained a clear insight into the nature of one class of nucleated holes. We present a model where nuclei, sites of high stress, are responsible for one class of holes in the dewetting film. These sites of high stress are intrinsic to a polymer melt that is prepared out of a solvent solution, e.g. dip coating, dip coating or spraying. By annealing the melt above glass transition temperature on top of a wettable substrate, the melt is able to release the stress and the polymer chains can attain their radius of gyration typical in the melt. After the transfer of the film onto a non-wettable substrate, number density of holes present after annealing was substantially reduced. The model is corroborated by the results of experiments with long-chained polymer molecules. Here, the number density of nucleation sites which are ‘deactivated’ by annealing increases with increasing polymer chain length, suggesting a direct proportionality of number of entanglements and stress. Moreover, our results suggest a way of stabilizing coatings for practical use by reducing the stress inside a film by means of annealing or by using short-chained polymers.

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\begin{thebibliography}{9}
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FIG. 1. Density of holes in 60 nm thick PS(51.5k) film as function of the annealing time. The solid line represents an exponential fit to the data.

FIG. 2. Density of nucleation sites \( n_s \) which are deactivated by annealing as function of film thickness. The solid line represents an exponential fit to the data.

FIG. 3. Density of nucleation sites \( n_s \) which are deactivated by annealing as function of molecular weight. The solid line represents a linear fit to the data.