Edge Effects in Single- and Multi-Layer Drying Coatings

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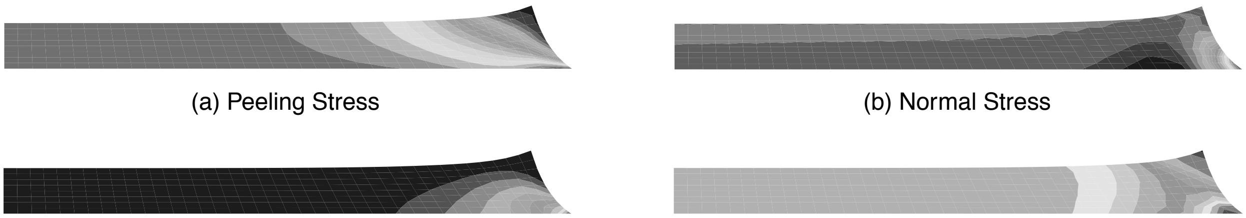
Introduction

Coatings are generally applied as liquid, then dried or cured to their final solid form. Whether by gelation or vitrification, the transition from liquid to solid can be approximated as occurring at a specific concentration — as is done in this research. Because solvent evaporation, polymerization, and cross-linking diminish the volume of the stress-free state of the coating, the current state shrinks insofar as it can. Ahead of the solidification front, the shrinkage produces flow in the still liquid coating; behind, it produces in-plane stress in the solid coating because its in-plane shrinkage is frustrated by adhesion to the substrate.

Far from the edge, non-uniformities in mass transfer, coating thickness, substrate profile, and other factors can lead to in-plane gradients in concentration, shrinkage and stress. Near the edge, drying is both top-down and edge-in, and can produce in-plane gradients even under uniform drying conditions. These gradients are two- and three-dimensional: one-dimensional models of drying and stress development are inadequate for understanding these gradients and their consequences.

Theory and Computation

Theory of two-dimensional drying is brought to bear on coatings applied as liquid that develop a moving solidification front on their way to their final dried solid form. The governing equations are those describing the solvent mass transfer by diffusion and convection; heat transfer to the coating by conduction, convection, and radiation; viscous flow in the liquid coating; appearance and subsequent movement of the solidification front; shrinkage and stress development in the solid coating; and the effect of falling solvent concentration on the coating's diffusivity, viscosity, elastic modulus, and yield stress.



(a) Peeling Stress

(b) Normal Stress

(c) Shear Stress

(d) Out-of-plane Stress

Figure 1: *Stresses near the edge of a single-layer fully dried coating. Stresses are highest near the edge and fall rapidly away from the edge; they are appreciable up to six thicknesses away.*

The governing equations are highly non-linear, and difficult if not impossible to solve in terms of algebraic functions. So the equations are solved numerically by a “method of lines:” Galerkin’s method with finite element basis functions in space, and finite-differencing of the time-dependent basis function coefficients. DASSL package (Brenan et al. 1989) ia used to solve the equations by a Newton’s method with secant-generated Jacobian (Salane 1986); and Hood’s frontal solver (Duff et al. 1986)is used to solve the linear matrix problem at each iteration.

The model system chosen resembles closely a polystyrene-toluene solution. The coating behaves like a Newtonian liquid before solidification, a neo-Hookean elastic solid after. If local stress in the solid coating exceeds the yield stress, the coating relaxes stress by plastic yielding of the stress-free state. Available experimental data on the concentration dependence of diffusivity, viscosity, and elastic modulus (Rauch and Köhler 2003, Gupta et al. 2000, Narukawa 2002) were fitted empirically and the curves were extrapolated to regions where data were not available. There appears to be neither experimental data nor theoretical framework about the concentration dependence of the yield-stress and post-yield viscosity. So the yield stress was taken to be a constant fraction of the elastic modulus, and post-yield viscosity was assumed to vary with composition as does the Newtonian viscosity.

Results and Discussion

Drying of already solidified two-layer coatings Solidified drying coatings that adhere to the substrate cannot shrink freely in the in-plane direction. The difference between the current state and the stress-free state of the coating is elastic strain to which stress is proportional; the proportionality factor is elastic modulus. At the edge, drying is both top-down and edge-in, and inherently two-dimensional. Non-uniform solvent removal there causes non-uniform shrinkage, and produces in-plane gradients in stress, as shown in Figure 1. Stress varies very close to the edge but only imperceptibly more than four to six thicknesses away. In-plane stress gradients can produce defects such as cockle; and the high tensile stress concentration at the edge can lead to delamination. Even uniform tensile stress, when excessive, can produce defects like curling and cupping, and

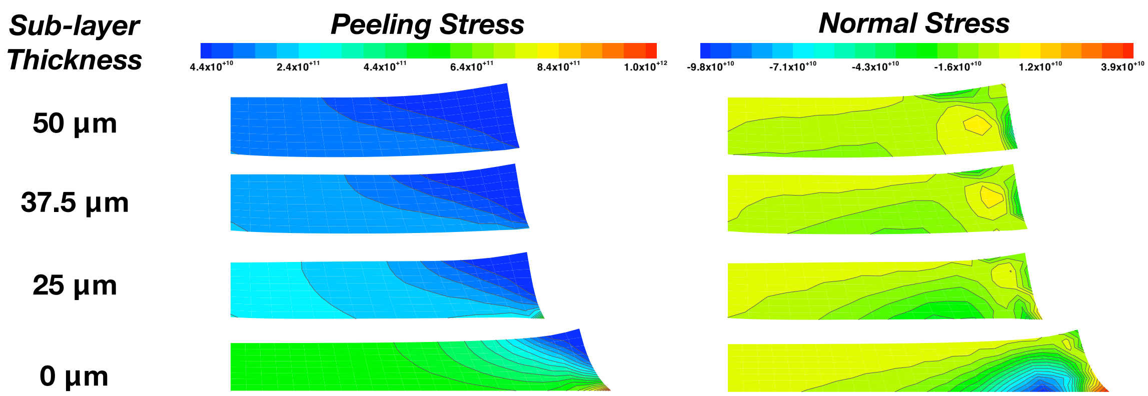


Figure 2: *Principal stresses in the upper layer of a solidified, fully dried two-layer coating(sub-layer not shown). Edge retraction grows with rising sub-layer thickness but is limited to near-edge.*

failures like cracking and crazing. If the coating yields, i.e. relaxes stresses plastically, the local stress in the coating falls to the yield value everywhere that value has been exceeded. Thus, plastic yielding reduces the level and variation of the concentrated stress near edges, and therefore the danger of defects and failures. Results show that high elastic modulus and high yield-stress raise the level of stress and in-plane stress gradients; high post-yield viscosity prevents the stresses from relaxing rapidly, producing a stress peak.

The high elastic modulus and yield stress of hard coatings make them susceptible to cracking and delamination. A method sometimes advocated to lower the overall stress is to apply a thin sub-layer of softer material between the hard layer and the substrate. The idea is that the softer sub-layer would allow the upper layer to retract more from the edge without significantly affecting the coating's functionality. Retraction of the upper layer's edge would allow its current state to be closer to its stress-free state, thereby lowering its strain and stress.

Figure 2 shows the effect of rising sub-layer thickness on the upper layer's edge retraction and stress concentration. The upper layer's elastic modulus, yield strength, and post-yield viscosity are five times greater than those of the sub-layer. The upper layer's initial thickness was 50μm in all cases; the sub-layer's thickness was varied from 0 to 50μm. With rising sub-layer thickness, the edge of the upper layer retracts more and its stress falls. However, edge retraction is limited and soon asymptotes. The retraction's effect is felt only near the edge, and falls quickly about four to six thicknesses away. Results indicate that the amount of edge retraction depends on the relative strengths of the two layers, and their relative thicknesses: weaker, thicker sub-layers allow the upper layer's edge to retract more but only up to a limit. So the method cannot lower stress overall, but it can at an edge, and thereby reduce the danger of nucleating delamination.

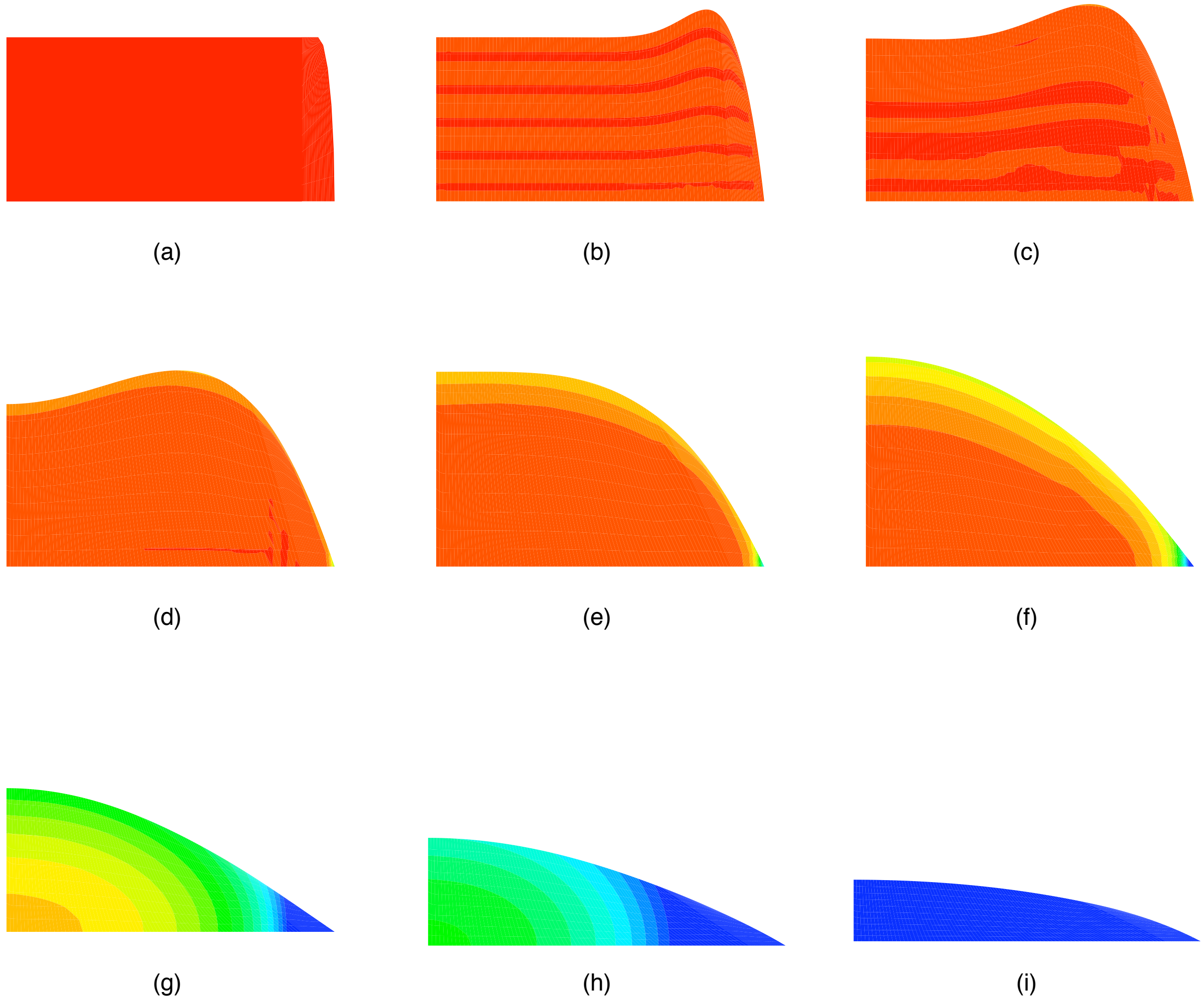


Figure 3: *Edge shape of a still liquid coating at different times of drying. Thickness is magnified ten-fold for better resolution. Solidification starts at the edge and moves toward the center of the narrow stripe of coating.*

Drying near the edge before solidification Whereas the concentration of stress in a solidified coating reaches no more than six thicknesses from the edge (as also noted by Tam (1997) and Lei (1999)), instances are numerous where the edge effects have intruded much farther. These can develop or begin developing when the coating is still liquid.

To examine this aspect, a flat liquid coating with an initially rounded edge, as shown in Figure 3(a) was modeled. If drying accompanies flow, the evolution of edge shape can be split into two stages: in the first, drying is insignificant and the volume of liquid is constant; in the second stage, drying becomes appreciable and the liquid volume shrinks continuously.

In the first stage, flow of the liquid coating is driven by capillarity, i.e. the gradient in curvature of the free surface. Liquid is driven away from the curved edge toward the middle, as shown in Figures 3(b) to 3(e), until ultimately the coating reaches its static equilibrium shape: the profile is an arc of a circle if the effect of gravity is negligible, as shown in Figure 3(f).

In the second stage, the loss in solvent volume causes the stress-free state of the liquid to shrink. The difference between the current state and stress-free state produces stress. The liquid flows if the stress exerts a net local force. The capillary pressure force is much larger than the force exerted by shrinkage: the liquid profile remains an arc of a circle. Because solvent evaporates, the arc's radius changes with time, as shown in Figures 3(g) to 3(i).

Only in stripe coatings can the liquid reach the arc shape. Otherwise, the coating solidifies before the capillary flow from the edge reaches the middle of the coating. The shape of the dried coating depends on the liquid shape at the time of solidification. Initial solvent concentration and drying conditions determine the time to solidify; resistance to flow determines the liquid edge shape. Flow resistance depends on the coating's viscosity, surface tension, and thickness. Solutions of the governing equations illustrate that higher viscosity, lower surface tension, and thinner coatings increase the flow resistance and in that way prevent the edge effect from going very far inward.

Summary and Conclusions

Stresses develop in a solidified drying coating due to its frustrated in-plane shrinkage. The effects of the coating's elastic modulus, yield strength, and post-yield viscosity on stress development and distribution can be analyzed and predicted. Edge retraction of the upper layer in a drying two-layer coating can reduce stress near the edge of a coating and so reduce the danger of nucleating delamination but cannot significantly affect stress in the rest of the coating.

Edge effects that arise from flow in the liquid phase intrude farther from the edge than those from shrinkage and stress. The final edge shape of dried coating depends on the edge shape of the liquid coating at the start of solidification, which in turn depends on initial shape, surface tension and the liquid coating's resistance to flow. The thinner and more viscous a coating, and the lower its surface tension, the narrower the edge region where thickness varies in an otherwise uniform coating.

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