Modeling Viscoelasticity and Stress Generation in Solidifying Coatings

Daniel J. O'Neal and A. V. McCormick

Coating Process Fundamentals Program
Department of Chemical Engineering & Materials Science
University of Minnesota, Minneapolis, Minnesota, 55414

Presented at the 14th International Coating Science and Technology Symposium,
September 7-10, 2008, Marina del Rey, California[1]

As a polymer solution coating solidifies by drying, or a coating of monomer or oligomer solidifies by polymerization and crosslinking reactions, it acquires an elastic modulus. Subsequent departure of solvent or advance of curing reactions causes the coating's elastic stress-free state to shrink isotropically but possibly nonuniformly. Adhesion to a solid substrate frustrates the solidification-induced shrinkage in the coating plane and produces elastic strain and, consequently, elastic stress in the coating. The magnitude and directions of the state of stress depend on the type of material, its physical property and shrinkage history, and the topography of the coated surface. Predicting stress generation can show how undesired defects are formed in the coating and can suggest avenues for optimizing the solidification process to minimize the residual internal stress and reduce defects.

The equation of momentum conservation, in dimensionless form, is

$$\frac{\mathrm{El}}{\mathrm{Sr}}\left[\tilde{\rho}\frac{\partial\tilde{\mathbf{v}}}{\partial\tilde{t}}+\tilde{\mathbf{v}}\frac{\partial\tilde{\rho}}{\partial\tilde{t}}\right]=\mathrm{El}\left[-\tilde{\rho}\tilde{\mathbf{v}}\cdot\tilde{\nabla}\tilde{\mathbf{v}}-\tilde{\mathbf{v}}\tilde{\nabla}\cdot\left(\tilde{\rho}\tilde{\mathbf{v}}\right)\right]+\tilde{\nabla}\cdot\tilde{\boldsymbol{\sigma}}$$

where the Elasticity number, El is the ratio of inertial to elastic forces and the Strouhal number, Sr, is the ratio of process to convective timescales. In a sample curing process, Sr = O(10^0) and

[1] Unpublished. ISCST shall not be responsible for statements or opinions contained in papers or printed in its publications.

El = O(10^{-11}) so the first two terms of the momentum conservation equation can be neglected and the equation reduces to the quasi-steady state form

$$\tilde{\nabla} \cdot \tilde{\boldsymbol{\sigma}} = \mathbf{0}$$

The Maxwell constitutive equation, the simplest viscoelastic constitutive equation that allows stress relaxation, is used as the constitutive equation for the solidifying polymer. This equation can be given in closed form, where the stress, strain, their time derivatives and physical properties are equated in a single equation.

$$\frac{\partial \boldsymbol{\varepsilon}}{\partial t} = \frac{1}{E}\frac{\partial \boldsymbol{\sigma}}{\partial t} + \frac{1}{\mu}\boldsymbol{\sigma}$$

With the quasi-steady state behavior of the equation of motion, the Maxwell constitutive equation can be rearranged to exploit easier computational techniques. The overall strain is split into three contributions; one for elastic, one for viscous relaxation, and one for stress-free shrinkage. The stress-free state is defined to be the material configuration where there is no elastic stress. This state changes as a curing reaction proceeds or as solvent evaporates. The constitutive equation can be split into two components of equal stress, an elastic and a viscous relaxation component. This method eliminates the time-dependence in the constitutive equation.

The two-dimensional system is discretized and solved using Galerkin's method with finite element basis functions and appropriate boundary conditions. After calculating the strain at a given time using the equation of motion and the constitutive equation, the relaxation strain is calculated using Euler's method and information from previous timesteps.

Using the method presented above, two-dimensional time dependent stress profiles can be calculated using a wide variety of input physical property data as well as for a variety of substrate topographies. The final internal state of stress depends on the physical property change with solidification, shrinkage, heterogeneity, and substrate topography. In general, residual stress is caused by competing factors; modulus increase and shrinkage tend to create stress while relaxation destroys it. By varying the rates of shrinkage, modulus development, relaxation time development, and the substrate topography, two-dimensional stress profiles are generated that allow us to see spatially and time-dependent states of stress in a coating. By comparing the stress profile from a uniform substrate to one that has a sharp topographic feature, the presence of the corner and valley create stress concentrations not seen in the uniform case. Presented are two-dimensional stress profiles for an ultraviolet light cured system that show how the curing time and substrate topographic height and length change the stress maximum magnitude and location. Such profiles can be used to optimize curing schedules and substrate geometry.