QUANTITATIVE PREDICTION OF STRESSES DURING THERMOSET CURE

Doug Adolf, Bob Chambers, and Steve Burchett
Sandia National Laboratories, Albuquerque, NM, 87185

Calculations are now routinely performed to predict the stresses in polymers employed as electronic encapsulants, printed wiring boards, and composite structural members. These calculations can predict stresses in nonisothermal operation which arise from mismatch in the polymer and component coefficients of thermal expansion. For crosslinking polymers such as epoxies, however, stresses evolve during cure due to reaction exotherms, cure shrinkage, and imposed deformations. Only recently has a formalism for calculating stresses in such systems been developed [1-4].

The calculation of the evolution of stresses during the cure of a crosslinking polymers is complicated by the change in viscoelastic properties with extent of reaction. For example, as the cure proceeds the shear modulus and longest shear relaxation time increase dramatically. Furthermore, since the glassy transition temperature increases with cure, all of the relaxation times increase due the increase in monomeric friction. Because the bulk modulus does not depend on the long-range network topology, it is far less sensitive to extent of reaction, so it is accurate to assume that the glassy and rubbery bulk moduli are independent of reaction. However, the shortest bulk relaxation time increases with reaction, as evinced by the increasing glass transition temperature.

Epoxies are thermorheologically simple. However, to apply this equation directly to curing resins we must introduce the further principle of chemorheological simplicity; that is, the normalized distribution of relaxation times does not change with extent of reaction. Experiments have demonstrated chemorheological simplicity for epoxy, siloxane, and urethane polymers [5-6].

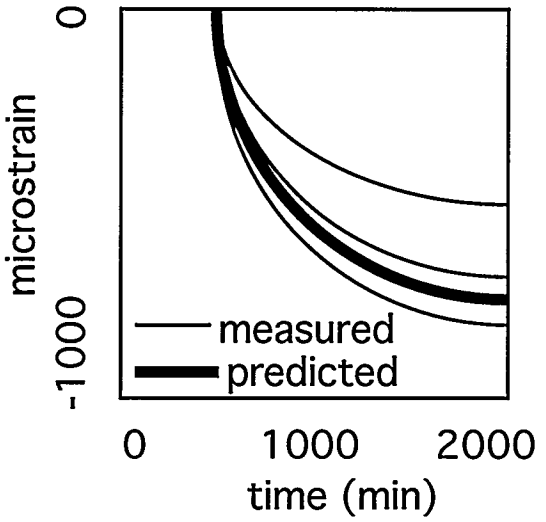
In our formalism, one calculates the extent of reaction for arbitrary thermal history, relates thermophysical properties to extent of reaction, and calculates the stresses from a consistent constitutive law. This procedure necessitates a knowledge of the reaction rate. If the epoxy vitrifies during cure, such as in the "B"-staging of printed wiring boards, the reaction will slow dramatically. A simple way to incorporate vitrification into the reaction rate law postulates that the characteristic reaction time constant is the sum of two independent processes, one arising from the intrinsic Arrhenius rate rate and the second arising from viscoelastic mobility [7].

To verify the formalism and the accuracy of our material characterization, we need to deform the

curing epoxy in various geometries and under different thermal profiles. In one such test, the experimental apparati consisted of two thin-walled aluminum tubes filled with epoxy which were cured nominally isothermally. One tube was instrumented with strain gauges to measure the hoop and axial strains at three points around the circumference of the middle of the tube. The second tube was fitted with thermocouples to measure the surface temperature histories of the outer and inner tube walls and in the epoxy near the tube center.

To calculate the cure stresses in this experiment, we needed to employ finite element codes. The thermal and extent of reaction time histories for each element were calculated separately first, since this problem could be decoupled from the stress calculations. We did not attempt to model convection in the oven, but, rather, set the outer wall temperature history of the aluminum tube equal to the measured history. The output from these thermal calculations was then fed to the stress codes. An iterative solution technique was employed, and unique routines were developed to solve this problem where such a large difference between the magnitudes of the deviatoric and bulk moduli existed.

The predicted and measured centerline hoop strains are shown below. Measured strains from the three gauges on an individual tube do not overlap due to slight tube out-of-roundness. The axisymmetric model predictions, of course, do not exhibit this scatter. Nevertheless, predictions and measurements agree.



We are now applying the formalism to encapsulated components of interest to Sandia. Not only can we calculate stresses for the current production cure schedule and propose new cure schedules which minimize these stresses, but we have gained unique insight into the epoxy behavior during cure which offers us paths to easier production and higher operational reliability.

(1) Martin et al *Phys Rev A* **39**, 1325, 1989.
(2) Adolf et al *Macro.* **23**, 527, 1990.
(3) Martin, Adolf *Macro.* **23**, 5014, 1990.
(4) Adolf, Martin *J. Comp. Mat.* **30**, 13, 1996.
(5) Adolf, Martin *Macro.* **23**, 3700, 1990.
(6) Adolf, Martin *Macro.* **24**, 6721, 1991.
(7) Matsuoka et al *Macro.* **22**, 4093, 1989.

DISCLAIMER