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Residual Stress Developed During the Cure of Thermosetting Polymers: Optimizing Cure Schedule to Minimize Stress

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Introduction

When thermosetting polymers are used to bond or encapsulate electrical, mechanical or optical assemblies, residual stress develops within the structure. This stress often affects the performance and/or reliability of these devices. Understanding the origins of the stress and how it evolves over time is key to defining strategies to minimize or alter the stress, with aims at eliminating impact on device performance.

Since stress can evolve during the manufacturing (e.g., cure), storage (e.g., thermal fluctuations) and testing processes, it is necessary to track stress during the lifecycle of a device in order to understand its impact on performance. Predicting stress over the entire lifecycle is a goal that many are striving towards. Constitutive frameworks[1-4] have enabled predictions of some aspects of the lifecycle and development and refinement of these tools continue. In this work, focus is on the manufacturing process. During the reaction of thermosetting polymers, chemical cross-linking generates volumetric shrinkage and an increase in the glass transition temperature (T_g) as the material transitions from a fluid to a “solid”, or gel. Additional crosslinking beyond gelation also drives an increase in the equilibrium shear modulus of the material. Methodologies to characterize the evolution of the material during reaction and to constitutively represent this evolution have been proposed.[5] Here, structural response tests aimed at designing cure schedules to minimize the residual stress developed during the cure process will be presented. These tests serve as a route to design cure schedules experimentally, even if all the details of the thermoset material are not know. The test can also be used to validate constitutive models that have been parameterized to represent the material evolution during cure. Of course, a model can explore parameter space much faster than experiments and point to optimum parameters that could be further validated with a subset of experiments. So development of both the experimental technique and predictive models is key to providing design tools to minimize the impact of stress on performance.

When setting out to optimize a cure schedule, one must first define “optimal” for the situation of interest. For instance, if throughput is the driving factor then a fast polymerization process may be the best solution. Since polymerization rate typically increases with temperature, an isothermal reaction at elevated temperature will complete the cure process faster as shown schematically in Figure 1.

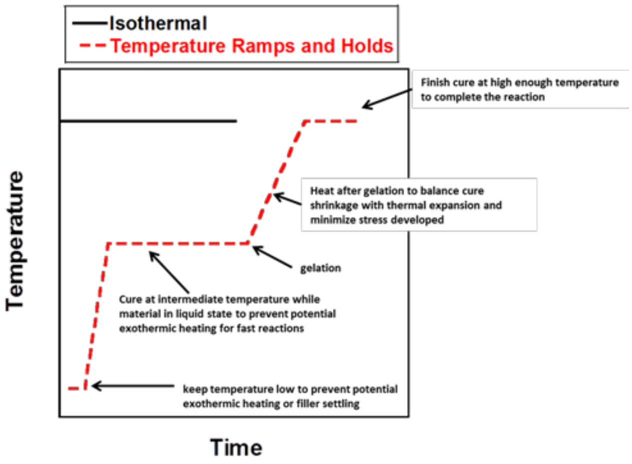

Figure 1. Potential temperature-time profiles for polymer thermoset cure schedules.

On the other hand, factors other than speed may drive the time-temperature profile in a different direction. Polymerization reactions are typically exothermic and if the reaction is extremely fast and/or the batch size is large then it may be necessary to keep the initial temperature low to prevent excess exothermic heating or even potential thermal runaway. At the lower temperature the viscosity of the material is also higher and may help prevent settling of any fillers in the mixture that have a mass density that varies from that of the resin. If residual stress is of concern, methodologies to lower the stress developed during the cure process could be proposed and tested. One hypothesis would be to balance some of the cure shrinkage of the material with thermal expansion by heating the material post-gelation, as illustrated in the “Temperature Ramps and Holds” scenario of Figure 1. This hypothesis will be tested in the following sections using a simple, yet elegant, structural response test.

Experimental

The thermosetting epoxy used in testing will be referred to as 828/DEA/GMB. The material is a mixture of EPON® Resin 828 (Momentive), a diglycidyl ether of bisphenol A, diethanolamine (Fisher Scientific) and D32 glass microballoons (3M). The chemical structure of the

828 resin and DEA curative are provided in Figure 2. The materials are mixed at a ratio of 100:12:28 parts by weight 828:DEA:GMB. During cure, the DEA first links to the epoxy via the secondary amine-to-epoxide reaction. This reaction is relatively fast and followed by the much slower reaction between the hydroxyl groups of the DEA and the epoxide. Both of these reactions are necessary to form the cross-linked network. Some material property characterization results of the curing and cured material are available electronically.[6]

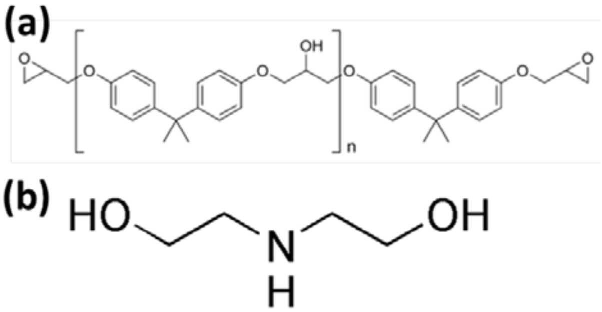

Figure 2. Chemical structure for (a) EPON® Resin 828 and (b) diethanolamine.

The structural response test used to assess the material during cure, the Thin-Disk-on-Cylinder, is shown in Figure 3. The geometry consists of a thick-walled 6061-T6 aluminum cylinder that is 3 in long and has a 1 in inner diameter (ID) and 1.5 in outer diameter. A thin, 0.024 in thickness, aluminum disk is secured to the bottom of the cylinder by a threaded cap that clamps the disk at the annular cross section of the cylinder. All inner surfaces, cylinder and thin disk, are blasted with 60 grit DURALUM® brown fused aluminum oxide (Washington Mills) using a Swam-Blast MV-21 (Crystal Mark). This surface preparation is to aid adherence of the thermosetting material to cylinder and thin disk. Maintenance of adhesion provides a stable boundary value problem for the test.

Figure 3. Thin-disk-on-cylinder (a) schematic, (b) individual parts and (c) assembled structure.

The test is instrumented with a CEA-13-062UW-350 Micro-Measurements® strain gauge (Vishay) on the exterior of the thin aluminum disk. The gauge is located at the center of the disk and produces a negative strain reading when the disk deflects inward towards the cylinder and a positive strain reading when the disk bulges outward away from the center [as illustrated in Figure 3(a)]. Temperature is also measured in three locations during a test: (1) the thermal chamber air, (2) the exterior surface of the cylinder (mold) and (3) the center of the cylinder (encapsulant).

Results and Discussion

Findings from an isothermal cure schedule will be shown and discussed, where both cohesive and adhesive failures of the 828/DEA/GMB material are observed. Time-Temperature profiles that prevent the material cracking and debonding will then be shown and a methodology to systematically alter the residual stress associated with the cure process will be demonstrated. The final residual stress in the system associated with cure results from a complex interplay amongst the cure shrinkage and the evolving modulus, T_g, and reference state. We'll show that even when a complete understanding of all these parameters is not available, primary factors that determine the residual stress state can be distinguished and used to control the end result.

Acknowledgements

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