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

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Abstract

When thermosetting polymers are used to bond or encapsulate electrical, mechanical or optical assemblies, residual stress, which often affects the performance and/or reliability of these devices, develops within the structure. The Thin-Disk-on-Cylinder structural response test is demonstrated as a powerful tool to design epoxy encapsulant cure schedules to reduce residual stress, even when all the details of the material evolution during cure are not explicitly known. The test's ability to (1) distinguish between cohesive and adhesive failure modes and (2) demonstrate methodologies to eliminate failure and reduce residual stress, make choices of cure schedules that optimize stress in the encapsulant unambiguous. For the 828/DEA/GMB material in the Thin-Disk-on-Cylinder geometry, the stress associated with cure is significant and outweighs that associated with cool down from the final cure temperature to room temperature (for measured lid strain, $|\varepsilon_{cure}| > |\varepsilon_{thermal}|$). The difference between the final cure temperature and the temperature at which the material gels, T_f-T_{gel}, was demonstrated to be a primary factor in determining the residual stress associated with cure. Increasing T_f-T_{gel} leads to a reduction in cure stress that is described as being associated with balancing some of the 828/DEA/GMB cure shrinkage with thermal expansion. The ability to tune residual stress associated with cure by controlling T_f-T_{gel} would be anticipated to translate to other thermosetting encapsulation materials, but the times and temperatures appropriate for a given material may vary widely.

Acknowledgments

JMK would like to thank Gary Pressly for the opportunity to initiate this work and for fruitful discussions around utilizing the findings and tailoring further experiments for application-based needs. Thanks also goes to Amy Kaczmarowski for support of this work, efforts to utilize the findings to alter production practices, and continued interest in further understanding the underlying material chemistry and physics that control how stress evolves during the cure process so that prediction of these effects may one day be possible. Kevin Long's technical review of the report is also greatly appreciated.

CONTENTS

FIGURES

1 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 over 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 continues. In this work, focus is on the manufacturing process. During the cure 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. The interplay of these effects and the boundary constraints (e.g., surface bonding) combine to define how the stress in the system evolves. Methodologies to characterize the evolution of the material during reaction and to constitutively represent it 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 known. 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 settings 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 1-1. 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 too 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 to lower stress 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 1-1. This hypothesis will be tested in the following sections using a simple, yet elegant, structural response test.

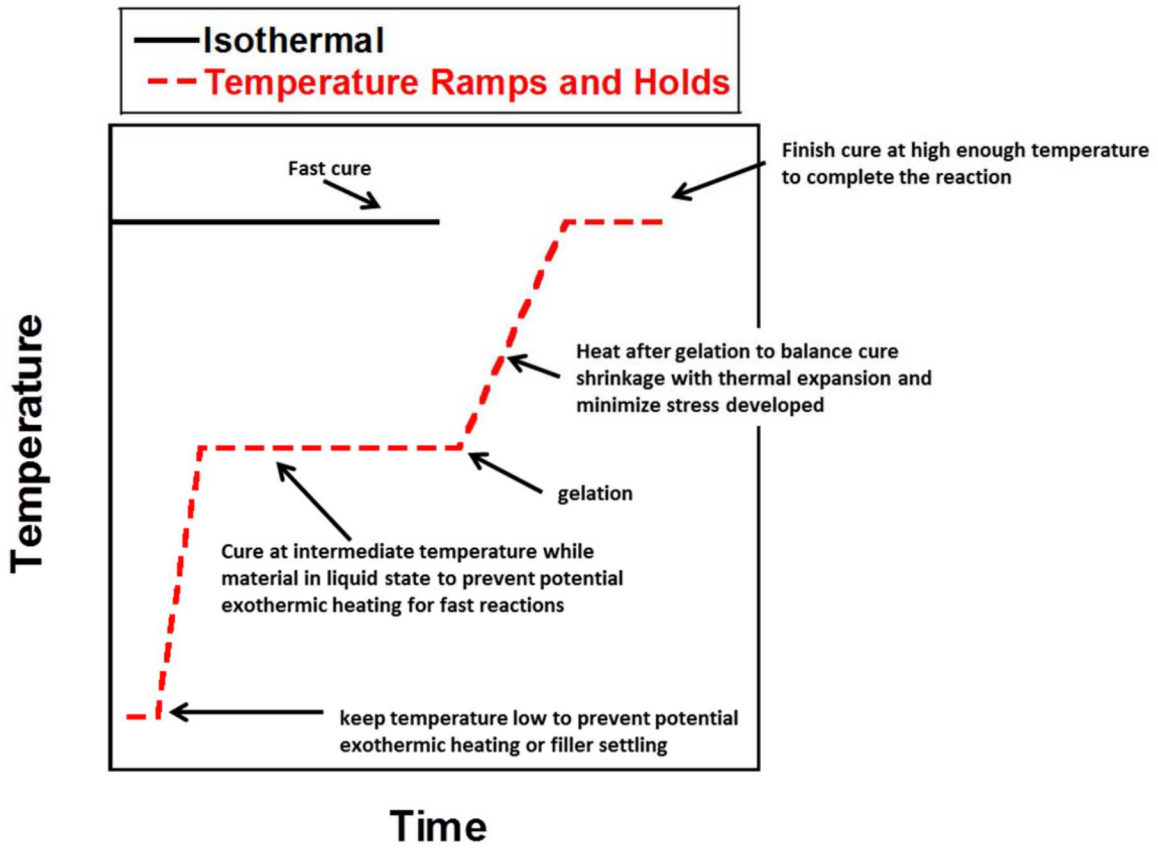

Figure 1-1. Potential temperature-time profiles for polymer thermoset cure schedules.

The remainder of this manuscript is organized as follows. In section 2, experimental methods and materials are described. The findings from the structural response tests are delineated in section 3 along with a discussion of the implications of the results. Finally, conclusions from the current work and an outlook on additional directions to explore are given in section 4.

2 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 (DGEBA), diethanolamine (Fisher Scientific) and D32 glass microballoons (3M). The chemical structure of the DGEBA resin and DEA curative are provided in Figure 2-1. 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 of epoxide with hydroxyl and other epoxide.[6-9] 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.[8]

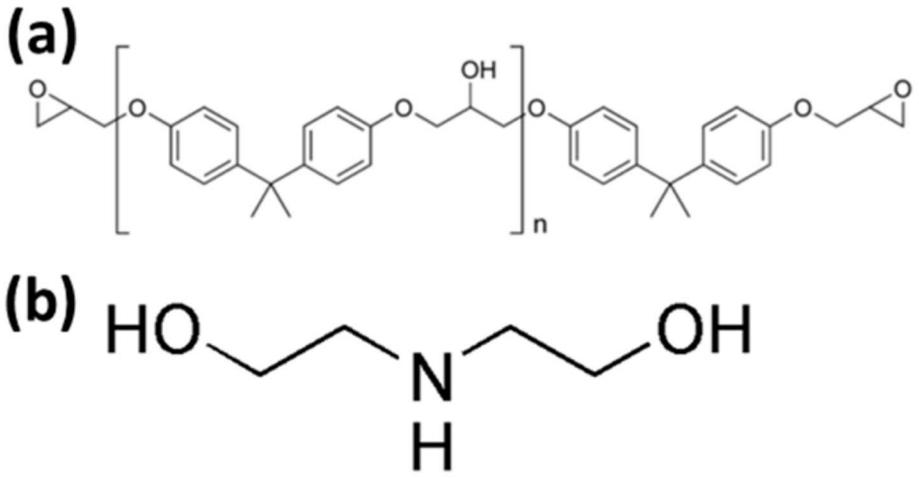

Figure 2-1. Chemical structure for (a) DGEBA and (b) diethanolamine (DEA).

The structural response test used to assess the material during cure, the Thin-Disk-on-Cylinder, is shown in Figure 2-2. The thin disk test technique was developed over 15 years ago to measure the effectiveness of mold releases used in epoxy encapsulation.[10] The test was designed to simplify the process of making and testing samples from that required for a previous test geometry, the kovar tube.[10,11] The new thin disk test method proved very successful for investigating the effects of encapsulant release with different surface conditions.

In some cases, however, the thin disk did not release from the encapsulant. While this was of limited utility to evaluate the mold release (other than it is not as effective as a material that enables release), the data from these in-tact (bonded) tests revealed valuable encapsulant curing information. Signatures of material gel times, the effect of temperature ramps during cure, and the completion of the polymerization reaction could all be resolved from the test. This technique was used to empirically develop a low stress cure for Sandia National Laboratory (SNL) electronic device encapsulation applications[12-14] and to eliminate the cumbersome gradient[13] cure setup that was previously used.

The geometry consists of a thick-walled 6061-T6 aluminum cylinder that is 3 in long (L) and has a 1 in inner diameter (ID) and 1.5 in outer diameter (OD). 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 roughened to aid adherence of the 828/DEA/GMB material to the cylinder and thin disk. The cylinder is blasted with 60 grit DURALUM® brown fused aluminum oxide (Washington Mills) using a Swam-Blast MV-21 (Crystal Mark). The blasting process is too severe for the thin disk. To prevent altering the thickness and geometry of the disk, it is roughened with 150-220 grit sandpaper. Maintenance of adhesion of the 828/DEA/GMB material to the cylinder and thin disk provides a stable boundary value problem for the test.

Figure 2-2. 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 2-2). 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). When testing replicate samples simultaneously, the duplicate sample is not instrumented with a thermocouple.

When completing an experiment, the following steps are followed: (1) instrument cylinder with strain gauge and thermocouples, (2) preheat constituent materials and cylinder to $T = 71°C$ (in some cases the GMB is preheated to $T = 107°C$, but this has not been determined to make a significant difference in the instrumented signals), (3) mix and degas constituents, (4) pour mixture into cylinder, (5) place cylinder into heating chamber and run programmed thermal profile. Strain and temperature measurements are logged throughout the process.

3 RESULTS AND DISCUSSION

Findings from a pseudo-isothermal cure schedule are shown in Figure 3-1. The test is described as pseudo-isothermal since at early times the temperature varies. First, the samples cool down during the handling associated with the experimental process. Later, the thermal chamber experiences a step increase in temperature, and exothermic heating associated with the reaction is notable at the time of the chamber step increase as well. Otherwise, the test is isothermal until the cool down to room temperature.

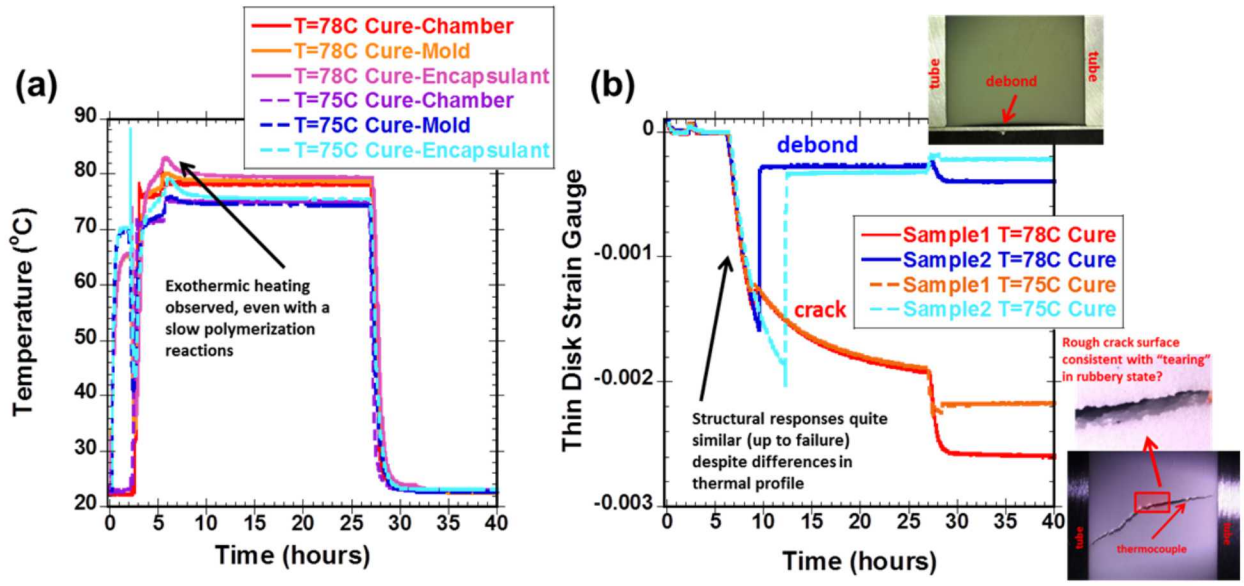

Figure 3-1. Thermal (a) and strain (b) profiles for pseudo-isothermal cure experiment.

Despite the differences in sample temperature, Figure 3-1(b) shows comparable lid deflection response amongst all samples at early time (< 8 hours). The strain signal remains at zero while the 828/DEA/GMB material is a liquid. After gelation, the material has a finite modulus and deflects the lid inward as shrinkage associated with the polymerization reaction occurs. The lid deflection initiates at approximately six hours. The six hour point is also when the 828/DEA/GMB material reaches a maximum in temperature (associated with exothermic heating above the chamber temperature), thus beyond this time cooling of the encapsulant (to the chamber temperature) from the maximum temperature will also lead to a thermal strain contribution to the inward deflection of the lid. The coincidence of the temperature maximum and the initiation of lid deflection also suggests that the gel point (t_{gel}) is correlated to the maximum rate of the polymerization reaction (t_{qmax}). This finding will be further explored during a detailed analysis of the reaction kinetics.[9] Soon after 8 hours, differences in the lid deflection responses amongst samples are noted. Two of the samples [red and orange curves of Figure 3-1(b) labelled "crack"] exhibit a small (< 0.0002) change in the direction of the lid deflection before additional inward deflection associated with 828/DEA/GMB cure shrinkage occurs. These samples included a thermocouple in the center of the cylinder to monitor the encapsulant material temperature. Post-test cross-sections of these samples revealed a cohesive

crack within the 828/DEA/GMB material in the vicinity of the thermocouple location. The crack within the encapsulant relieves a portion of the force pulling on the lid, as the "free surface" of the encapsulant is now transferred from the top to the center of the cylinder. That relief in force manifests the change in direction of lid deflection. Note that the decrease in magnitude of the strain signal associated with the cracking occurs over ~ ½ hour and suggests that the crack did not occur instantaneously. Rather, an initiation and propagation process over this course of time is the likely explanation. Examination of the crack surface [see Figure 3-1(b)] reveals a rough texture consistent with a "tearing" of the material in the "rubbery" state versus a smoother crack surface that would be anticipated from fracture of the material in the "glassy" state. This is consistent with the reversal in lid deflection direction being associated with cohesive cracking that occurs during the polymerization process, as during cure the temperature is above the glass transition temperature of the encapsulant material. The continued inward deflection of the lid after the cracking process suggests that the 828/DEA/GMB material is still constrained by the walls and lid of the cylinder. The continued cure and shrinkage of the material applies additional force on the lid and results in the additional inward deflection, the free surface boundary condition in the test has just moved closer to the lid.

The other two samples [blue and cyan curves of Figure 3-1(b) labelled "debond"] do not exhibit the small change in direction of lid deflection that the samples containing thermocouples did. Rather, these samples demonstrated a continued inward deflection of the lid beyond the time at which the thermocoupled samples experienced cracking. At a later time and larger magnitude lid strain, these samples without thermocouples exhibit a discontinuity in the lid strain. The strain "jumps" to a near zero value and remains there through the duration of the elevated temperature reaction process. Post-test cross-sections of these samples revealed a debonding of the 828/DEA/GMB encapsulant from the thin disk, but no cohesive cracking in the 828/DEA/GMB like was apparent in the thermocoupled samples. This suggests that the presence of the thermocouple causes a stress concentration that exceeds the strength of the encapsulant material and leads to the cohesive failure within the 828/DEA/GMB. Without the stress concentration in the material associated with the thermocouple, the force applied to the lid during cure is able to reach the debonding level before a material cohesive failure. Neither of these failure mechanisms, cohesive cracking in the encapsulant material or debonding of the encapsulant material from mating surfaces, is desired in applications where the encapsulant is depended upon for high voltage dielectric protection and/or mechanical shock and vibration protection. The following paragraphs will demonstrate methodologies to avoid these failure mechanisms and reduce the stress associated with the cure process.

In Figure 3-2, findings from a more sophisticated thermal profile during the cure process are shown. In this case, the pre-gel reaction is executed at a lower temperature and a post-gel thermal ramp is used to elevate the temperature to the final cure temperature. Prior to gelation, the strain signals show only small deviations from zero associated with the temperature changes in the experiment. Post-gelation, the strain signals exhibit a very "rich" behavior compared to the isothermal tests, which will now be described. For the $T = 40°C$ pre-gel hold experiment, lid deflection (inward towards the cylinder) initiates during the $T = 40°C$ hold and shows a local minimum when the thermal ramp initiates. This local minimum can be understood in terms of the competition between cure shrinkage of the 828/DEA/GMB material and the thermal

expansion associated with the temperature change. The thermal expansion rate of the 828/DEA/GMB material associated with the ~ 4°C/hr temperature ramp exceeds the cure shrinkage rate associated with the reaction kinetics at T = 40°C. Thus, the lid begins to deflect back to the zero strain gauge reading position at the initiation of the thermal ramp. During the thermal ramp, a local maximum and another local minimum are observed. As the temperature initially increases in the T = 40°C to T = 70°C range, the reaction rate of the material increases[7-9] while the thermal expansion rate stays the same (due to the constant temperature ramp rate, assuming that the thermal expansion changes in the material associated with cure are negligible). Eventually, the reaction kinetics become fast enough that the cure shrinkage rate outweighs the thermal expansion rate and results in the local maximum in the strain signal. Even though the temperature continues to increase throughout the thermal ramp, this does not result in a continuous increase in the polymerization rate for the 828/DEA/GMB material. The reaction rate shows a peak at ~65% conversion and decreases with further reaction extent.[9] At some point, the decrease in reaction rate with reaction extent outweighs the increase in reaction rate with temperature and the reaction rate slows during the thermal ramp of the cure experiment. This process leads to the local minimum in the strain signal towards the end of the temperature ramp, where the thermal expansion rate once again outweighs the cure shrinkage rate. A final local maximum in the strain signal is noted at the completion of the thermal ramp, and a minor, slow decrease in the strain signal is observed during the final T = 70°C hold. The local maximum is associated with the end of the thermal expansion and the completion of small amounts of additional reaction during the T = 70°C hold. A final lid deflection associated with the cool down to room temperature is observed at the end of the test.

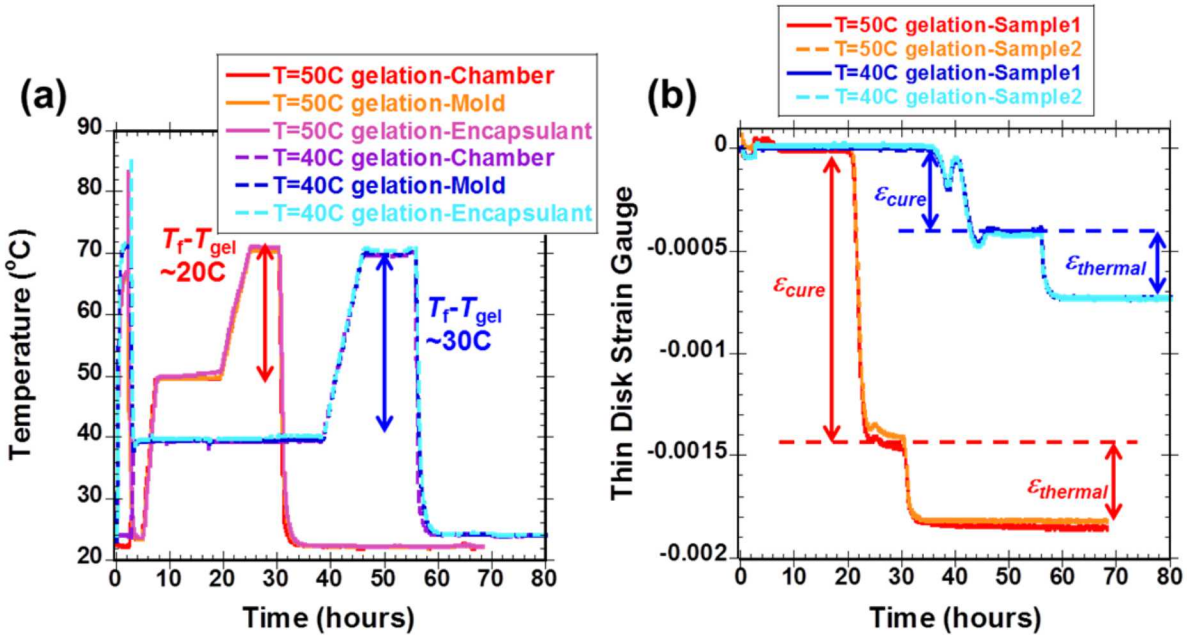

Figure 3-2. Thermal (a) and strain (b) profiles for more sophisticated thermal profiles during cure.

The strain signal behavior for the T = 50°C pre-gel hold experiment is very similar to the T = 40°C pre-gel hold experiment. A notable difference between the two tests is the lack of a local minimum in the strain signal at the initiation of the thermal ramp for the T = 50°C pre-gel hold experiment. In this case, the thermal ramp initiated (at ~19.5 hours) before the initial deflection of the lid (at ~20.5 hours). Indeed, the temperature has already increased to ~55°C before lid deflection begins. By comparison, by the time that the T = 40°C pre-gel hold experiment reaches T = 55°C the reaction rate has become fast enough that the cure shrinkage rate outweighs thermal expansion rate and the lid is deflecting inward.

The temperature ramps and holds cure profiles shown in Figure 3-2 prevented the encapsulant cohesive cracking and/or debonding observed in the isothermal cure profiles examined in Figure 3-1. The ability to tune the residual stress associated with the cure process is also apparent from Figure 3-2. While both cure processes in Figure 3-2 result in the same extent of reaction and give the same physical properties of the material, completing the gelation at T = 40°C reduces the total lid deflection at the end of cure by more than a factor of two from that when gelation occurred at T = 55°C. The additional lid deflection associated with cooldown is independent of the precursing cure schedule, which is not surprising since the change in temperature during cooldown is equivalent and physical properties of the encapsulant have not significantly changed. Thus, the difference in lid deflection between these two cure schedules remains the same after cool down as it was at the end of cure.

Another observation that can be made from Figure 3-2 is that the stress associated with the reaction process is significant. Take the T = 50°C pre-gel hold experiment for example. The cure process accounts for more than ¾ of the total lid deflection (i.e., cool down to room temperature from the final cure temperature accounts for < ¼ of the total lid strain), and some of the cure shrinkage is balanced with thermal expansion. This finding was not anticipated. Indeed, in many cases when modeling encapsulation stress the cure process is ignored and the system is assumed stress-free until the cool down from the cure temperature. Certainly, in the case of the Thin-Disk-on-Cylinder geometry filled with 828/DEA/GMB this assumption is a poor one.

The ability to tune the residual stress associated with the cure process is further illustrated in Figure 3-3. In this case, the pre-gel hold temperature is varied from T = 40°C, to T = 45°C, to T = 50°C. The final cure temperature, T_f, is held constant at T = 70°C. Thus the temperature difference between where gelation occurs, T_{gel}, and where the polymerization reaction is completed is systematically changed. This is illustrated in Figure 3-3(a). Admittedly, gelation did not always occur before thermal ramp initiation for the pre-gel hold temperature of T = 50°C. This resulted in $T_f - T_{gel} < 20$°C for some cases and a broader distribution of strain readings for this thermal profile compared to the other thermal profiles that it is depicted with in Figure 3-3. The strain gauge readings from multiple tests for each of these thermal profiles are shown in Figure 3-3(b).

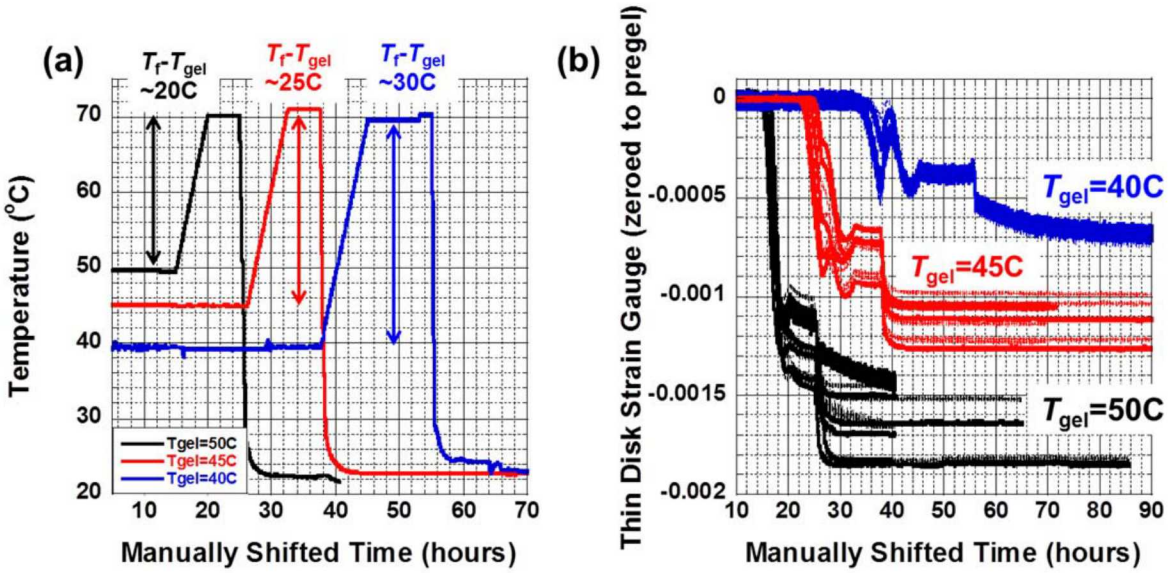

Figure 3-3. Thermal (a) and strain (b) profiles for systematic changes in the difference between the temperature at which the encapsulant gels and the temperature at which the polymerization reaction is completed.

First note the distinct differences in the strain responses amongst the thermal profiles. Not surprisingly, as the pre-gel hold temperature increases the time at which the lid deflection initiates decreases. This is a result of the increase in the isothermal reaction kinetics of the polymerization process with temperature in the T = 40-50°C range.[7-9] Assuming the reaction extent at gelation remains constant, the time differences amongst lid deflection initiation could be accounted for by the time differences to reach the extent of reaction at which the material gels. This will be examined more closely in a follow-up communication. The key difference amongst the strain responses for identifying the minimization of stress associated with cure in the final "product" is the strain at the end of the T = 70°C hold. The absolute value of this quantity monotonically changes with the pre-gel hold temperature as ~0.0004, ~0.0007-0.009, and ~0.001-0.0015, for pre-gel hold temperatures of 40, 45, and 50°C, respectively. So by changing the temperature range over which the sample is ramped post-gelation by as little as 10°C, the strain reading from the deflecting lid can be changed by almost a factor of 4. This is significant, and is distinguishable within experimental uncertainty of the test.

Considering experimental uncertainty, it should be noted that the strain data of Figure 3-3(b) includes not only sample-to-sample and batch-to-batch variability, but also temperature variability of the thermal chambers used to execute the cure profile. This structural response test has been found to be particularly sensitive to even small changes in temperature for the 828/DEA/GMB material. An example of this is demonstrated in Figure 3-4. A difference of approximately 3°C in the pre-gel hold temperature changed the time at which lid deflection initiated by over an hour. Thus, while the chamber 2 specimens exhibited initiation of lid deflection at ~51°C, lid deflection of the chamber 1 specimens did not initiate until after the

thermal ramp started and temperature had reached ~57°C. This delay in the lid deflection initiation also had implications on the rate at which the deflection occurred and the final deflection reached. With the deflection initiating at a higher temperature for the chamber 1 samples, the polymerization rate of the 828/DEA/GMB material was faster and resulted in a faster lid deflection rate than for the chamber 2 samples. The higher lid deflection initiation temperature and lower final cure temperature for the chamber 1 specimens also means that there is less opportunity for thermal expansion of the encapsulant during cure to "counteract" the cure shrinkage of the material. This appears to be a primary factor in determining the total lid deflection of the samples at the end of cure and after cool down, when considering both Figures 3-3 and 3-4. While the detailed answer is certain to be more complicated (the residual stress in the system associated with cure will result from a complex interplay amongst the cure shrinkage, material confinement, and the evolving modulus, T_g, and reference state), the ability to reduce stress associated with confined cure by balancing cure shrinkage with thermal expansion is convincing. For instance, take into consideration that chemical cross-links are formed at lower temperatures with the $T = 40°C$ pre-gel hold temperature and yet this cure schedule results in the lowest lid deflection at the end of cure at $T = 70°C$. Similar statements can be made about the chamber 2 specimens from Figure 3-4. So the difference between the gel and final cure temperatures appears to be dominant over, say, the temperature at which chemical cross-links are formed, in terms of defining the final stress state of the system.

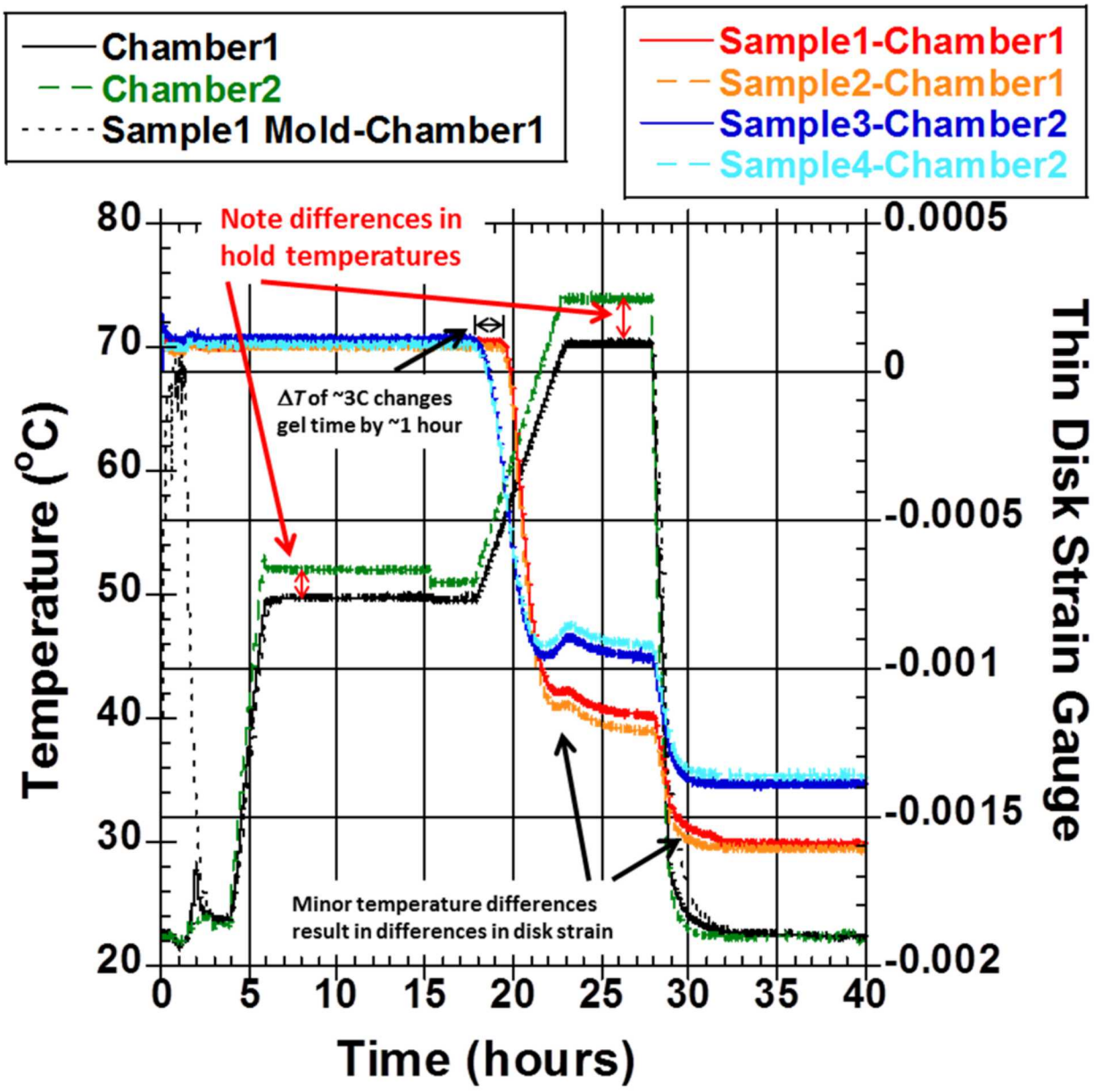

Figure 3-4. Thermal and strain profiles for cure schedules that the exhibit small changes in the temperature profile.

In Figure 3-5, an additional example of the temperature sensitivity of the Thin-Disk-on-Cylinder structural response test for the 828/DEA/GMB material is given. In production of encapsulated parts, temperature variations of a thermal chamber during the cure schedule are often allowed. It is common to allow temperature tolerances of +/- 3°C during a cure schedule. To demonstrate the impact of a scenario where cure temperature varied but stayed within this allowed tolerance, the $T = 45$°C pre-gel hold cure schedule was examined with both a +/- 3°C change applied to the complete cure profile.

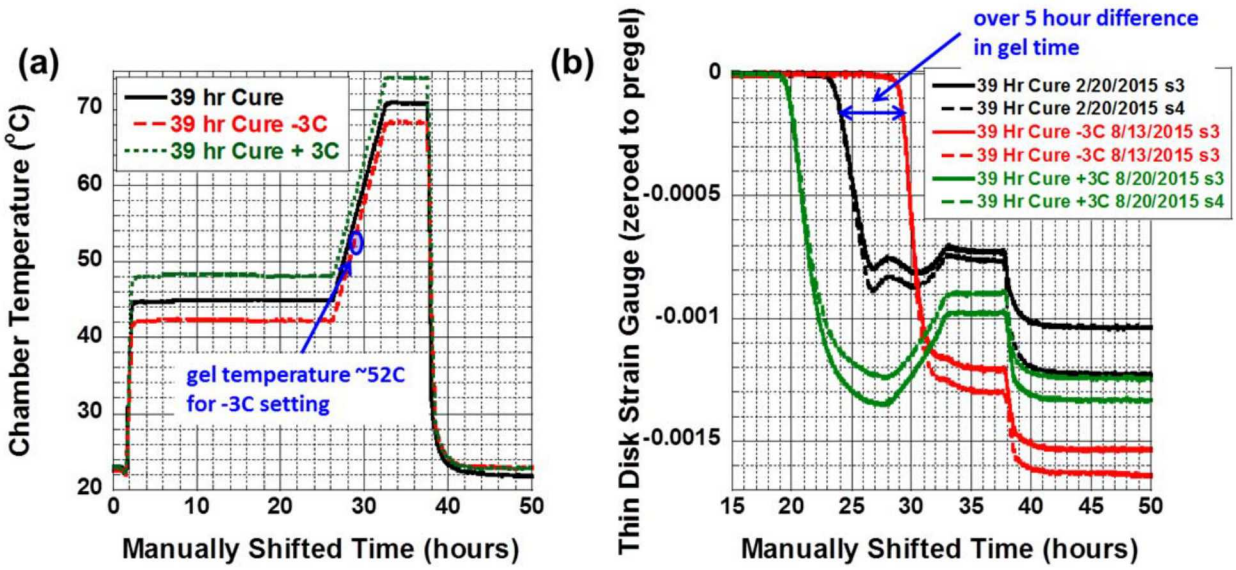

Figure 3-5. Thermal (a) and strain (b) profiles for +/- 3°C change applied to the complete cure profile of the *T* = 45°C pre-gel hold cure schedule.

Not surprisingly based on the findings of Figure 3-4, the 3°C offset in cure profile makes significant changes to the lid deflection strain signal. The -3°C temperature offset results in the lid deflection initiation occurring after the thermal ramp begins. The temperature has reached T = 52°C (from its T = 42°C hold value) by the time lid deflection is observed. This reduces the T_f-T_{gel} value defined in Figure 3-3 from the nominal (+/- 0°C) cure profile by 7°C, and the absolute value of the strain associated with lid deflection at the end of cure is larger (~0.00125 versus 0.00075). On the other hand, lid deflection initiation occurs during the temperature hold for the +3°C temperature offset. In this case, T_f-T_{gel} remains equivalent to that of the nominal (+/- 0°C) cure profile. Despite T_f-T_{gel} equivalence though, the strain associated with lid deflection at the end of cure is not equivalent. This illustrates that factors other than T_f-T_{gel} contribute to the final stress state in the system. The role of all factors will not be completely elucidated in this manuscript, but are of interest to understand in our continuing research. Coming back to production sensitivities, if an optimized cure schedule means minimizing stress then it would be desired to tighten temperature tolerances in this scenario. Both the +/- 3°C offsets result in an increase in the residual stress associated with cure.

4 CONCLUSIONS

The Thin-Disk-on-Cylinder structural response test has been demonstrated as a powerful tool to design epoxy encapsulant cure schedules experimentally, even when all the details of the material evolution during cure are not explicitly known. The reproducibility of the measured strain signals enables time-temperature cure profiles to be distinguished within experimental uncertainty. The test's ability to (1) distinguish between cohesive and adhesive failure modes and (2) demonstrate methodologies to eliminate failure and reduce residual stress, make choices of cure schedules that optimize stress in the encapsulant unambiguous. In addition, the sensitivity of the test to even small changes in the temperature (at least for the 828/DEA/GMB material) and the "rich" strain profiles observed for the "temperature ramps and holds" cure schedules examined herein provide insights into the interplay amongst the parameters that define the residual stress in the system as well as a dataset for validation of models that can represent the evolution of the 828/DEA/GMB material during cure.

For the 828/DEA/GMB material in the Thin-Disk-on-Cylinder geometry, the stress associated with cure is significant and outweighs that associated with cool down from the final cure temperature to room temperature. The difference between the final cure temperature and the temperature at which the material gels, T_f-T_{gel}, was also demonstrated to be a primary factor in determining the total lid deflection and hence the residual stress in system associated with cure. Increasing T_f-T_{gel} leads to a reduction in cure stress that is described as being associated with balancing some of the 828/DEA/GMB cure shrinkage with thermal expansion. While this simple interpretation of the results is attractive, it would be naïve to think that it is the whole story. Examining additional materials and additional test geometries in similar experiments is anticipated to further elucidate how factors other than T_f-T_{gel} contribute to the final stress state in the system.

As may be anticipated, the choice of an optimum cure schedule involves trade-offs amongst key parameters. For example, the price of low residual stress in these experiments is an extended cure time. Other trade-offs not explicitly shown here include keeping stress low at the final room temperature state versus keeping stress low at earlier stages of cure when the encapsulant is "weakest".[15] Of course, where application materials and geometries vary from the 828/DEA/GMB and Thin-Disk-on-Cylinder examined here, "optimum" cure schedules will vary too. For instance, the ability to tune residual stress associated with cure by controlling T_f-T_{gel} would be anticipated to translate to other thermosetting encapsulation materials, but the times and temperatures appropriate for a given material may vary widely. Changing geometry (particularly the amount of confinement experienced by the thermosetting material) may have a significant effect on the ability to control residual stress associated with cure by changing the time-temperature profile too. In a relatively unconfined geometry, even isothermal cure profiles may only generate small amounts of residual stress compared to that generated during temperature changes (due to thermal expansion mismatches between the encapsulant and its confining interfaces). These are areas of interest for continued research investigations.

The ultimate goal of this work would be to enable prediction of how the residual stress associated with cure evolves based on a knowledge of the underlying material chemistry and physics involved. Some success towards this goal has been achieved,[5] but there is much more to do in order demonstrate a robust predictive capability.

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