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Effects of Varying the Cure Profiles of an Epoxy-amine System

by

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Abstract

The cure of an epoxy prepolymer with an amine hardener induces stress in thermosetting systems. The extent of residual stresses in the cured epoxy-amine thermosets are dependent on several factors; one of which is the cure profile utilized. The effect of cure profile on cure induced stresses of an epoxy-amine thermoset was examined in the current study. A difunctional epoxide based on diglycidyl ether of bisphenol-A (DGEBA) and a tetrafunctional amine curative were used to conduct this study. Two cure profiles were selected to prepare samples of varying degrees of stress in the cured thermosets. The first was constant heating and the second was stop heating before post cure. Thermo-mechanical analysis (TMA) was conducted to observe the dimensional change as a result of the presence of different degrees of residual stresses in the cured thermosets. The effect of cure-induced residual stress on mechanical properties, modulus, strength, and fracture toughness was also evaluated. It was observed that the samples cured with the constant heating cure profile incurred larger residual stresses as observed by thermo-mechanical analysis. However, mechanical properties of thermosets obtained from both the cure profiles were not affected significantly.

Key Words: Thermosets, Stress, Properties, Crosslinking, Polymer

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Chapter I

Introduction

1.1 Epoxy thermosets

Epoxy thermosets have wide application in almost every aspect of material science ranging from medical to military applications.[1-3] Their high strength and corrosion resistance make them desirable for use in components such as aircraft parts and automotive panels. A wide range of commercially available epoxy resins and hardeners enable users to realize the gamut of flexible thermoplastics to brittle thermosets in a variety of applications.

The most widely used cure mechanism for epoxy resins is via the reaction of epoxide groups with amine curatives. By choosing appropriate amine and epoxy resins, the crosslink density of the resulting thermoset can be controlled as desired. In many cases, complete curing of the epoxy-amine system requires the use of high temperatures for a certain period of time; with an autoclave offering the option of pressure as an additional cure variable. During cure, the viscosity of the epoxy-amine blend increases gradually, transforming the liquid reactants to a solid (vitrification) to yield a glassy-like, amorphous solid.

As the physical state of the epoxy-amine system changes during cure, it experiences compressive stresses due to volume shrinkage and expansive stresses due to the elevated temperature. Ultimately, compressive stresses dominate and are retained upon complete cure. These residual stresses affect the material performance and can cause premature failure.[1,3] Varying the cure profile (cooling before post curing, continuous post curing, different cooling rate, etc.) could alter the amount of residual stress in the system. For instance, a longer cure profile (higher cooling rate and cooling before post-curing) lowers the residual stress in the system.[4] This study was designed to determine the differences in residual stress of an epoxy-amine system cured through two different cure profiles and its effect on macroscopic performance properties, if any. A bifunctional diglycidyl ether of bisphenol-A (DGEBA) based epoxy prepolymer and a tetra-functional amine were chosen for the study.

1.2 Characterization of thermal residual stresses

Several approaches have been proposed to measure residual stresses, such as Fiber Braggs Grating (FBG), fiber stress analysis, and substrate deformation[1, 3-4, 5, 6, 7], with the majority of these studies using FBG sensing. In FBG sensing, a single optical fiber is embedded in the uncured epoxy. Light is passed through the fiber and the scattering of the light by the epoxy is measured. As cure progresses, the light scattered by the epoxy-amine will change, causing one particular peak, the Braggs peak, to shift from its original location. This shift along with the peak intensity is used to determine the evolution of stresses in the epoxy during cure.

In fiber stress analysis, a single fiber is attached to a load cell and a known amount of tension is applied to it. The epoxy is then cast around the fiber, and the changes in tension on the fiber as the epoxy cures are measured by the load cell.[4] As the temperature rises, thermal expansion causes a decrease in tension on the fiber. On the other hand, increased crosslinking results in compressive stresses, which increases the tension on the fiber. Madhukar *et al.*[4] were able to thermally control the stress on the fiber during cure. For example, if the stress on the sample began to decrease, indicating that thermal expansive stresses were increasing, the heat input was lowered, and vice versa for an increase in compressive stresses. The results of their study showed that, though the stress on the fiber changed dramatically throughout the cure, the final stress was only slightly different than the initial stress, indicating that thermal residual stresses within the particular epoxy system being studied were minimal.

A method to measure thermal residual stresses based on substrate deformation determines the effects of compressive stresses and thermal shrinkage within an epoxy sample based on the degree of bending it induces in a metal substrate. A schematic representation of this method is depicted in Figure 1.1, where the orange top layer is the cured epoxy and the black bottom layer is the substrate. Aluminum is typically used as the substrate since it deforms easily under the compressive stresses of the curing epoxy. The increase/reduction in the amount of flex indicates an increase/decrease in both compressive and expansive stresses. When these stresses are equal, the substrate will have little to no deformation.

Figure 1.1. Depiction of deformed epoxy/substrate.

1.3 Current deficiencies

A change in cure profile is likely to alter the mechanical performance of a cured system. Increased internal stresses are reflected in thermal transitions as measured via dynamic scanning calorimetry (DSC) and thermogravimetric analysis (TGA). These stresses may also affect the mechanical performance, which can be modeled using flexural, tensile, and fracture toughness testing.

1.4 Research goals and objectives

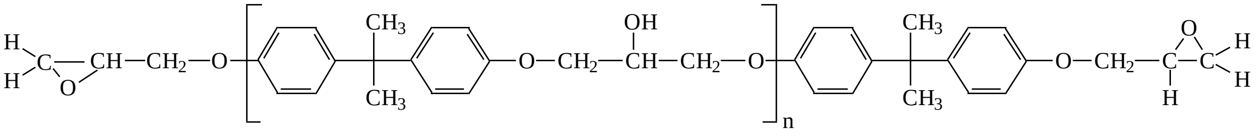
The proposed study will study the effects of varying cure profile on thermal residual stresses of an epoxy-amine network based on DGEBA and 4,4'-diaminodiphenylmethane (4,4'-DDM). The standard cure profile for this system is four hours at elevated temperature followed by cooling to ambient temperature and then a post-cure of two hours at a temperature above the glass transition temperature (T_g). The modified cure profile will four hours at elevated temperature followed immediately by two hours at a temperature above the T_g. The thermal residual stresses of the system from the standard cure profile will be compared to those of a modified cure profile. Residual stresses in the system will be determined via thermomechanical analysis (TMA). TMA detects dimensional change of materials that occur with change in temperature. Materials containing varying level of stresses are expected to exhibit differences in their dimensional change, particularly around their T_g.[8] The effect of stress on mechanical properties will be evaluated in terms of their tensile modulus, flexural modulus, and fracture toughness.

Chapter II

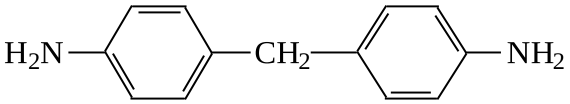
Experimental

2.1 *Introduction*

The epoxy used in the proposed study is Epon® 828, provided by Momentive. Epon 828 is based on DGEBA and has a reported epoxide equivalent weight of 185-192 g/equiv. Prior to use, the epoxy equivalent weight of Epon 828 was determined via ASTM D 1652-97 to be 188.72 g/equiv. The epoxy will be cured with 4,4'-DDM, provided by Sigma Aldrich (97% pure as received). The amine hydrogen equivalent weight (based on 97% purity) of 4,4'-DDM is 51.10 g/equiv. The structures of both these compounds are depicted in Figure 2.1.



DGEBA-based epoxy prepolymer, Epon 828 (n = 0.12)



4,4'-DDM

Figure 2.1. Structures of Epon 828 and 4,4'-DDM.

2.2 *Sample preparation*

Prior to blending Epon 828 with 4,4'-DDM, the epoxy prepolymer was degassed in a vacuum oven at 100 °C for an hour to remove any volatile materials. After degassing, a stoichiometric amount of epoxy was weighed into a beaker and placed in an oil bath set at 75 °C. The equivalent amount of 4,4'-DDM was weighed and added to the beaker under mechanical agitation (Table 2.1). Stirring was continued for 30 minutes and the transparent hot solution was placed in a vacuum oven set at 90 °C for 5 minutes to remove air bubbles. The degassed hot solution was cast onto silicone molds and placed in an oven at 90 °C. Silicon molds were designed to obtain dynamic mechanical analysis (DMA), tensile, flexural, and fracture bars. TMA specimens were prepared from tested fracture bars.

Table 2.1 Epoxy-amine formulation

Reagent	Amount (g)	Number of equivalents
Epon 828	90.51	0.48
4,4’-DDM	24.49	0.48
Total	115.00	0.96

2.3 Curing of epoxy-amine blend

The cure conditions for this study were selected from a previous kinetic study.[8] Figure 2.2 displays Near infrared (NIR) spectra of a stoichiometric blend of Epon 828 and 4,4'-DDM cured at 90 °C for four hours and 200 °C for four hours. The epoxy, primary amine and secondary amine peak intensities decreased while the -OH peak intensity increased as a function of time and temperature due to the formation of secondary hydroxyls from the epoxy-amine reaction. Disappearance of epoxy, primary amine and secondary amine peaks indicated complete cure of the Epon 828 - 4,4'-DDM blend.

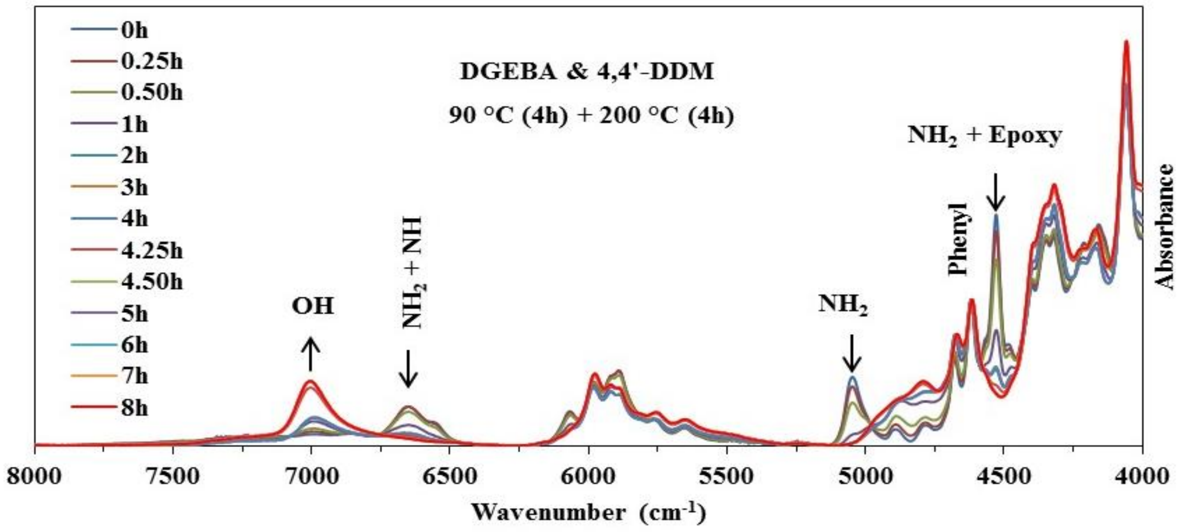


Figure 2.2. Near IR spectra of stoichiometric blend of Epon 828 and 4,4'-DDM during cure at 90 °C for 4 hours and 200 °C for 4 hours.
[Reproduced with permission from reference 8]

Pramanik *et a.l*[8] calculated the concentration and conversion of epoxy and amine functional groups during cure of Epon 828 with 4,4'-DDM. Figure 2.3 shows concentration and conversion of epoxy, primary amine, secondary amine, and total amine hydrogens of Epon 828 and 4,4'-DDM stoichiometric blend during cure at 90 °C for four hours and post-cure at 200 °C for four hours. Conversion of each functional group (epoxy, primary amine, and secondary amine) was determined from the near IR spectra by applying Lambert-Beer's law.[8] It was noticed that epoxy conversion proceeded to 88.85% in two hours during cure at 90 °C. Beyond this point, the epoxy-amine reaction proceeded very slowly for the next two hours due to diffusion limitation resulting from vitrification of the system. When the temperature was increased to 200 °C, the remaining epoxy reacted completely in one hour. It was observed that epoxy and total amine conversions proceeded at the same rate throughout the cure, which in turn indicated that epoxy reacted with amine (primary and secondary) only. This suggested that Epon 828 and 4,4'-DDM stoichiometric blend does not undergo side reaction like epoxy-hydroxy etherification when cure at 90 °C and post cure at 200 °C. It is therefore expected that Epon 828 and 4,4'-DDM stoichiometric blend will react completely at the cure schedule of 90 °C for four hours and 200 °C for two hours and was chosen for our study.

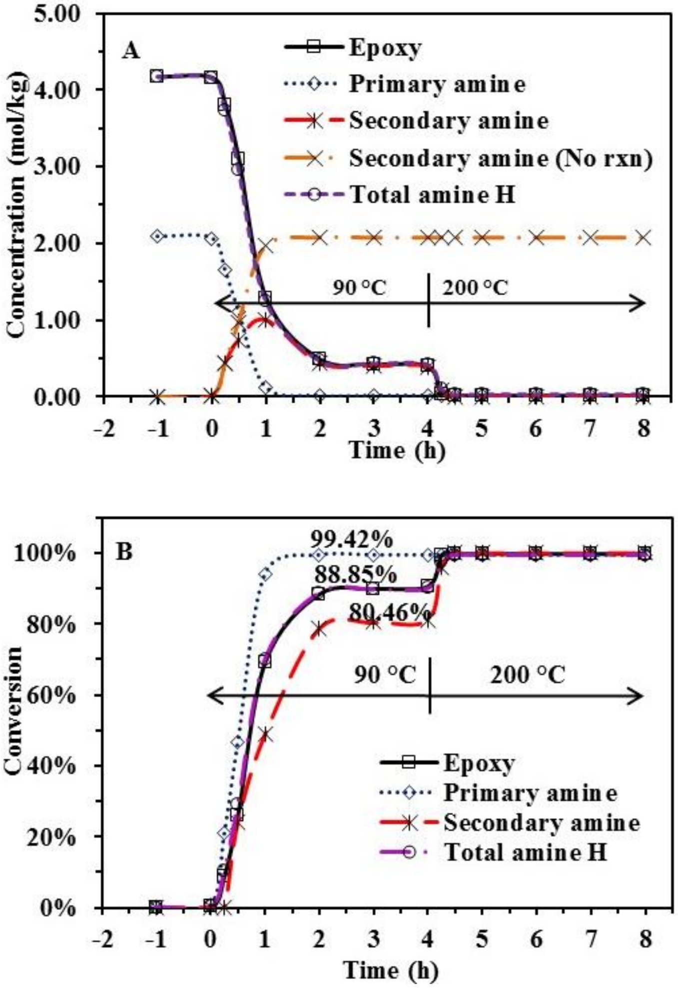


Figure 2.3. Concentration (A) and conversion (B) of epoxy, primary amine, secondary amine, and total amine hydrogen of Epon 828 & 4,4'-DDM stoichiometric blend during cure at 90 °C for four hours and post-cure at 200 °C for four hours.
[Data at -1h represents the pre-blend concentration where extent of reaction is zero and it was not measured via NIR; data at 0h represents first data obtained via NIR spectra of blend/solution after specimen preparation. Reproduced with permission from reference 8]

To observe how the cure profile induces different amounts of stresses in an Epon 828 - 4,4'-DDM system, two cure profiles were selected; one being the standard cure profile used for this epoxy-amine system and the other being a modified cure profile. The first cure profile employed a four hours dwell at 90 °C followed by a slow cool down to ambient temperature and a two hour dwell at 200 °C. The samples were then slowly cooled again to ambient temperature. For the second cure profile, the sample was cured for four hours at 90 °C and post-cured immediately at

200 °C for two hours without an intermediate cooling step. It was hypothesized that the modified cure cycle will result in higher stresses in the samples.

2.4 *Processing and testing of samples*

Prior to test, cured samples were machined using a flat-plane mill to ensure that each sample has a uniform dimension and surface. After machining, the samples were sanded using a very fine grit sand paper to obtain a smooth surface. Any air pockets along the edges of the sample were sanded away to prevent the sample from prematurely failing along those points. After machining and sanding, the sample dimensions were measured. Figure 2.4 depicts the schematic representations of the various sample bars that were tested.

For tensile samples, dimensions were ~3.08 mm thick and ~12.65 mm wide. Tensile tests were conducted as per ASTM D 638-03 and measured on a MTS Insight instrument with a load cell of 10 kN (2,248.09 lbf) and operated at a crosshead rate of 1.27 mm/min. To measure the tensile modulus, a sensor (extensometer) was attached to the sample to measure sample elongation up to 2% strain. Strain beyond 2% moves outside the elastic response of the sample and causes plastic deformation. The slope of the stress vs strain plot was reported as modulus. After testing for tensile modulus, the samples were placed back in the equipment to measure their tensile strength. The maximum stress required to break the sample was reported as the tensile strength (in MPa).

Flexural test was conducted as per ASTM D 790. Flexural bars were 3.00 mm thick and 13.00 mm wide. Support span distance was maintained at 16 times the thickness of the flexural bars. Flexural properties were measured on a MTS Insight instrument equipped with a load cell of 10 kN (2248.09 lbf) operating at a crosshead speed of 5 mm/min. Flexural modulus was calculated from the slope of stress vs strain curve.

Fracture toughness was tested according to ASTM D 5045-99, with sample dimensions being 7 mm thick and 15 mm wide. A notch of 0.45 times the width was cut into the center of the sample using a drilling bit. A crack was then initiated at the tip of the notch using a fresh razor blade and a dropped weight. Measurement was conducted on a three-point test setup with a crosshead speed of 1.27 mm/min on a MTS Insight instrument.

DMA bars of thickness ~1.00 mm and span of ~ 6.00 mm between sample clamps were tested on a DMA Q800 from TA Instruments operated at a ramp rate of 2 °C/min and a test frequency of 1.0 Hz.

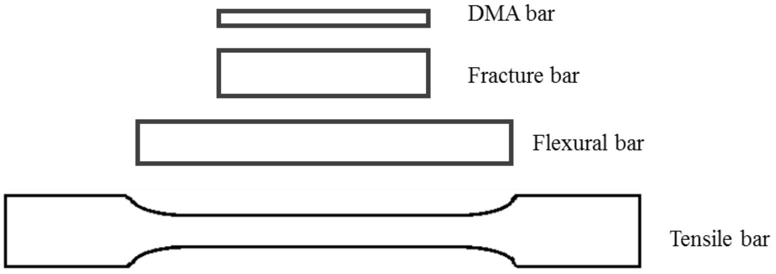


Figure 2.4. Depiction of Sample Bars for Mechanical Testing.

Thermomechanical properties (change in dimension vs temperature and T_g) of cured samples were measured. Residual stresses can cause a sample to expand and contract differently with changes in temperature.

2.5 Analysis of results

The data obtained from each test of the two different cure profiles was processed using Microsoft Office Excel. Data from the average (along with standard deviation) of at least three specimen were reported.

2.6 Timeline

Sample preparation was begun in January of 2013, with initial testing being conducted immediately following. All initial testing was completed as of February 2013. Repeats of TMA samples were cast and tested between the months of February and May 2013. In October 2013, a second set of samples were produced and testing was conducted. The final test data were collected in January of 2014.

2.7 Summary of Expected Results

Jyotishkumar *et al.* reported that a cure profile that applied constant heating to a sample produced a larger relaxation at the T_g, and attributed it to a larger build-up of residual stresses.[9] It is expected that the modified cure profile used in the present study will yield similar results. TMA data should show a larger relaxation in stresses for the modified cure. It is also expected that the sample containing higher residual stress will have poorer mechanical properties.

Chapter III

Results and Discussion

3.1 Thermal results

Residual stress was analyzed via TMA using samples cut from fracture bars. Fracture bars were cut down to 2.5 mm thick for TMA analysis. Dimensional change in the TMA samples was measured on a Q400 Thermomechanical Analyzer operated at force of 0.02 N, heating rate 5 °C/min via the employment of an expansion probe with a temperature range of 25 °C to 250 °C. The release of thermal residual stresses at the T_g of each cure profile was calculated. Figure 3.1 depicts the thermal response of both cure profiles.

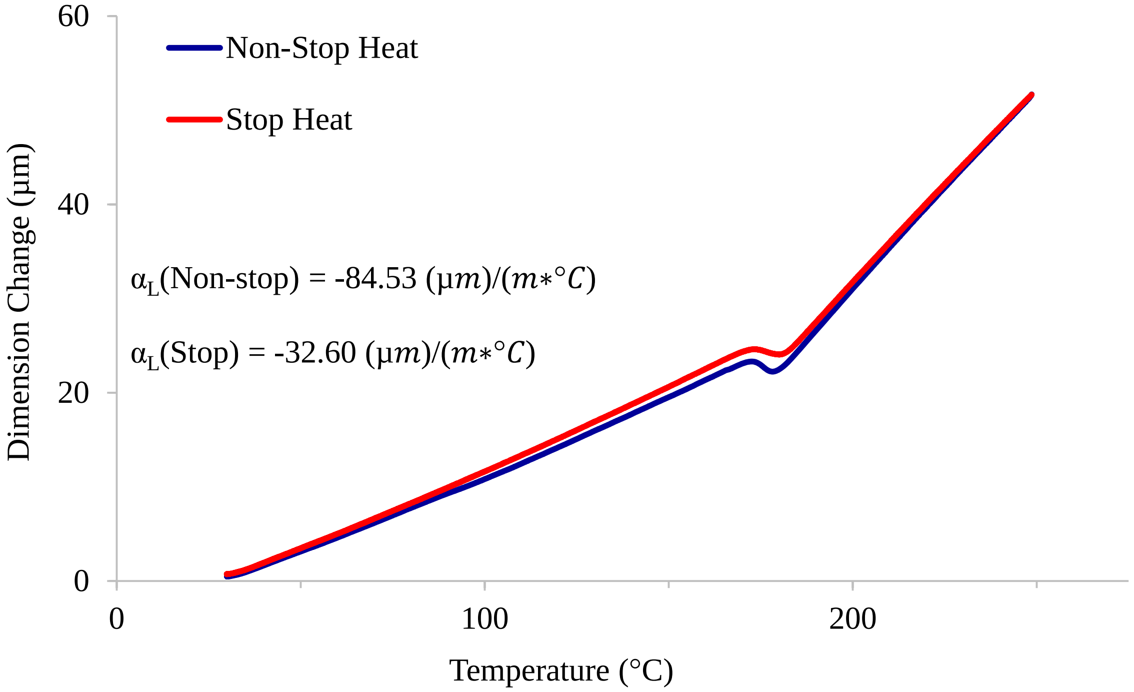


Figure 3.1. TMA Heat Cycle 1.

It was noted that the modified cure profile (labeled non-stop) showed a significant drop in dimensional change at the T_g. This drop is attributed to either a release of thermal residual stresses, or a release of volatiles such as trapped moisture. To examine this further, NIR spectroscopic measurement were conducted on the samples and the resulting spectra are shown in Figure 3.2. The peak at 5230 cm^{-1} in the sample is due to the presence of trace amounts of moisture. The spectra also showed that samples from both cure profiles contained the same negligible amount of moisture.

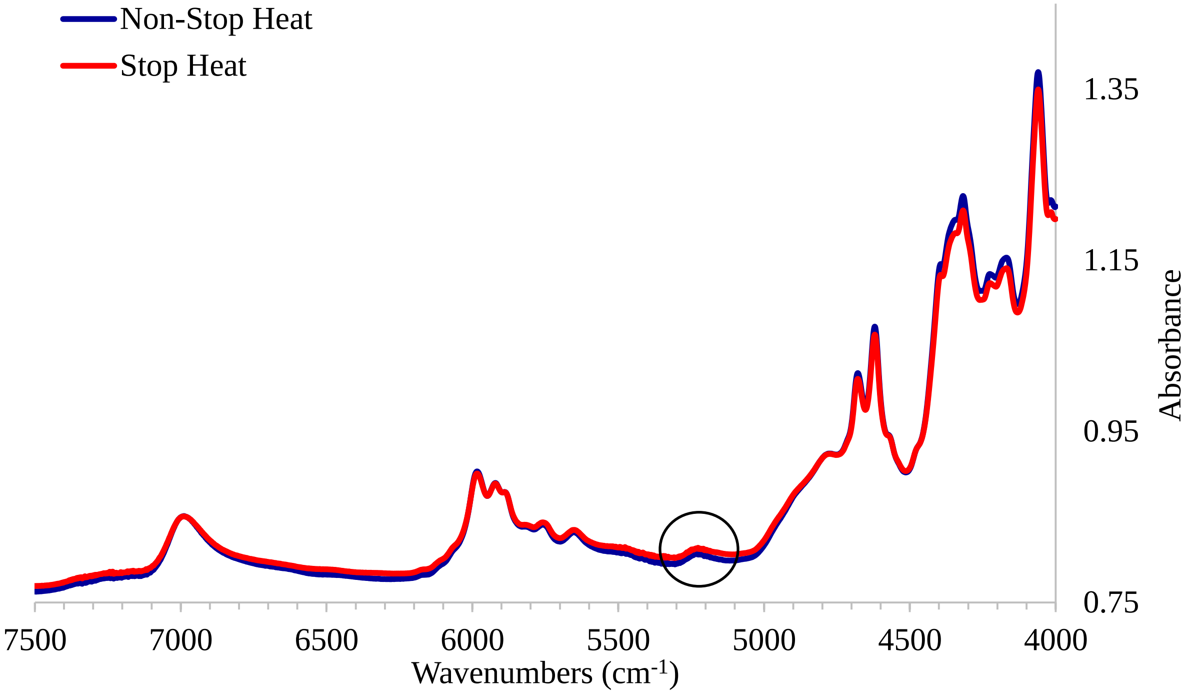


Figure 3.2 NIR Spectra.

The TMA results suggest that the modified cure profile imparted higher thermal residual stresses into the sample than the conventional cure profile. The sample from the modified cure profile is likely to have greater free volume, which in turn would cause greater dimensional change than the sample from the conventional cure profile. It should be noted that the machining step may be releasing residual stress to some extent. The milling process induces a significant degree of heat due to friction between the milling bit and the sample, and is expected to induce partial relaxation in the sample. It is possible that unmilled samples would have exhibited a greater dimensional change at the T_g than was observed in the milled samples.

The coefficient of linear thermal expansion (α_L) for both cure profiles at their T_gs further demonstrated the effects of residual stress in the sample. The non-stop curing profile exhibited a larger negative α_L, indicating greater relaxation and higher stress release.

It is possible to erase the thermal history of a sample by annealing it at a temperature above the T_g that is low enough to prevent sample degradation. This can be observed in TMA through employment of a heat-cool-heat cycle. The results of the first heat cycle are shown in Figure 4.1. The second heat cycle, which showed the erasure of thermal history for both cure profiles, is shown in Figure 3.3.

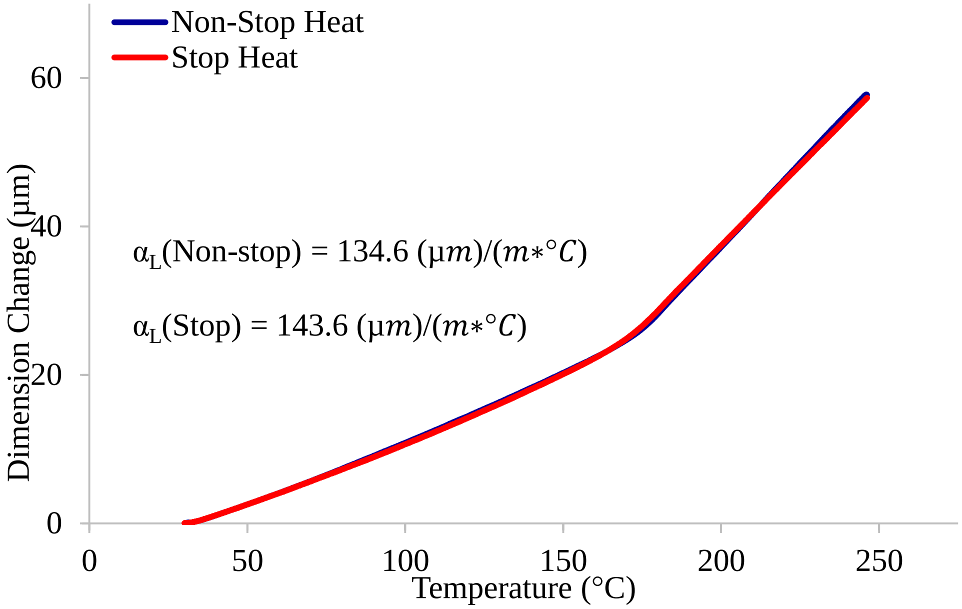


Figure 3.3. TMA Heat Cycle 2.

3.2 Mechanical properties

Table 3.1 summarizes the results of mechanical properties for fracture, flexural, and tensile tests. Although the dimensional change observed via TMA was sufficiently different between the two cure profiles, the mechanical properties (tensile, flexural and fracture toughness) were not different statistically.

Table 3.1 Mechanical Properties

	Non-Stop Heat	**Stop Heat**
Tensile Strength (MPa)	65.45 ± 4.72	66.46 ± 5.21
Tensile Strain at Break (%)	5.93 ± 0.68	6.03 ± 1.17
Tensile Modulus (GPa)	3.21 ± 0.30	2.91 ± 0.30
Flex Modulus (GPa)	2.77 ± 0.17	2.93 ± 0.38
Flex Strain at Break (%)	7.07 ± 0.79	6.28 ± 0.71
Flex Strength (MPa)	101.2 ± 3.32	98.03 ± 6.33
Fracture G_{IC} (J/m^2)	219.71 ± 81.81	220.47 ± 87.96
Fracture K_{IC} (MPa*$\sqrt{m}$)	0.76 ± 0.15	0.76 ± 0.18

Dynamic Mechanical Analysis (DMA) determines the elastic (storage) and damping (loss) properties of a viscoelastic material. An average of two results for each specimen was reported (Figure 3.4). It is seen that storage modulus did not differ much between the two cure profiles. However, a slight difference was observed in the tan δ peak, i.e., T_g.

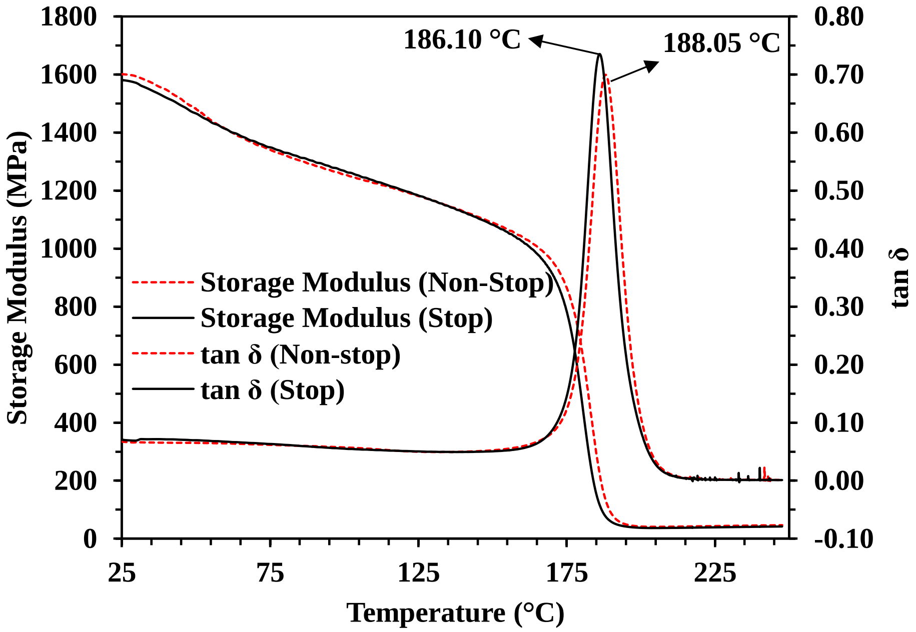


Figure 3.4 DMA results.

3.3 Conclusions

The objective of this study was to examine the effects of varying cure profile on the residual stress and mechanical performance of an epoxy-amine system based on Epon 828, a difunctional epoxide, and 4,4′ - diaminodiphenylmethane, a tetrafunctional amine curing agent. The results showed that the residual stress in each cure profile did affect the thermal response of the samples as seen by stress relaxation via TMA, but did not significantly affect the mechanical properties of the samples. Jyotishkumar *et al*. reported that a difference between cure profiles was noticeable via TMA but there was not an observable difference between mechanical properties.[9] The same trends were observed in this study.

It is possible that epoxy-amine systems with higher average functionality would have exhibited significant differences in residual stress due to their higher degree of crosslinking. It is also proposed that increasing the cure time could also have imparted higher residual stresses.

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