

# The Effects of Cure Schedule on Properties of Glass-Fiber Reinforced Epoxy Matrix Composites

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## APPROVAL PAGE

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## **ABSTRACT**

Two different two-component resin systems were cured, via Differential Scanning Calorimetry, for the times recommended by their respective manufacturers. The resin cure schedules were designed to simulate typical and attainable processing conditions; they were cured at 120°F, 140°F, and 160°F, and in-mold post-cured at 200°F, 230°F, and 260°F. The resulting scans were then compared to a baseline cure for each resin system, consisting of two heating-cooling cycles at a constant rate of temperature change. These baseline cures were then used to determine the percent cure of each sample and the shift in glass transition temperature between the baseline cure and the samples. Analysis showed that all samples were fully (100%) cured. This was confirmed by producing partially cured samples for each resin system, which all used a lower curing temperature than the regular samples. The first resin system displayed 91.8% cure with a curing temperature of 167°F, while the second system showed 92.1% cure at a curing temperature of 150°F. Statistical analysis showed that there was no significant effect of cure temperature or in-mold post-curing temperature on the shift in glass transition temperature of the resin, nor was there any significant interaction between the two factors. The glass transition temperature of resin A was 154.5°F with a standard deviation of 13.9°F, while the glass transition temperature for resin B was 164.4°F with a standard deviation of 22.0°F. Tensile samples were made using the same processing temperatures, but were also thoroughly mixed and degassed to reduce porosity once the resin was poured into the mold. The samples were then tested and analyzed based on tensile strength; the average tensile strength of the resin A samples was 60.44 MPa with a standard deviation of 2.40 MPa, and the average tensile strength of the resin B samples was 63.19 MPa with a standard deviation of 5.87 MPa. It was discovered that the cure schedule did not have a statistically significant effect on the tensile strength of the resin.

**Key Words:** Materials Engineering; Epoxy Resin; DSC; Glass Transition Temperature; Aptera Motors, Inc.; Aptera 2e, Composites, Cure Schedule,

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## **PROBLEM STATEMENT**

The automotive industry has long been a prominent contributor in emission of pollutants into the atmosphere. However, various technological advances have been made to allow for the production of reliable and convenient electric vehicles. Materials must be developed to meet the stringent weight, cost, and mechanical constraints of these vehicles. One promising group of materials used for this application is polymer matrix composites (PMCs); they unite the strength of the reinforcing fibers with the ease of molding and low density of the matrix. These composites are sensitive to the kinetics of how the matrix is cured and solidified around the reinforcing fibers; a relatively long curing time allows for a better fiber-matrix interface, but costs more to produce. Since the cost of producing a vehicle correlates to the price of the vehicle for consumers, the curing time should be minimized to both reduce the cost and increase market share as consumers prefer to purchase these vehicles over more expensive gasoline-powered models. Optimizing the curing process with respect to these parameters and controlling its effects on the properties of the PMCs for use in an electric automobile, like Aptera Motors, Inc's 2e, is an important area of investigation, and is the basis of my senior project.

## **BACKGROUND**

### *Fiber-Reinforced Composites*

Glass-fiber reinforced polymer (GFRP) panels are ideal for cars. When compared to steel, they have a higher strength-to-weight ratio, allowing for lighter weight body panels, and are easier to make into complex shapes, permitting more aerodynamic shapes to be manufactured. These PMC panels are much more cost effective than their carbon fiber-reinforced counterparts, and when coupled with an epoxy matrix, they become affordable alternatives to other polymers and metals without a significant loss in mechanical properties.

PMCs achieve the low density and ease of production that polymers possess. This ease of production is because the initial components, the resin and hardener, are liquid, allowing the two components to fill complex molds without necessitating high temperatures or pressures, as other materials like metals would need (further complicating production).

More importantly, however, is that PMCs have vastly improved mechanical properties when compared to unfilled polymers; this is due to the fibers that reinforce them. These properties are improved due to the difference between the elastic modulus of the fiber material and the matrix material. Since the reinforcing fibers have much higher moduli than the matrix they fill, they will develop higher stresses under equivalent strain once under load. Under uniaxial longitudinal loading, the stress state follows Hooke's law.

$$\sigma = E \epsilon \Rightarrow \epsilon = \sigma / E$$

Since the load on the composite must be taken up by both the fibers and the matrix, the stress in the composite can be rewritten as

$$P_{comp} = P_{fib} + P_{mat} \Rightarrow \sigma_{comp} A_{comp} = \sigma_{fib} A_{fib} + \sigma_{mat} A_{mat}$$

Dividing both sides by  $A_{comp}$  and using  $v_{fib} = A_{fib}/A_{mat}$ , The equation reduces to



$$\sigma_{comp} = \sigma_{fib} v_{fib} + (1 - v_{fib}) \sigma_{mat} \quad \text{Eq. 1}^1$$

Therefore, adding fibers to a polymer matrix can vastly improve the strength of the composite. Similarly, using Hooke's law and the fact that  $\epsilon_{comp} = \epsilon_{fib} = \epsilon_{mat}$ , an equation for the longitudinal tensile modulus is created:

$$E_L \epsilon_{comp} = E_{fib} \epsilon_{fib} V_{fib} + (1 - v_{fib}) E_{mat} \epsilon_{mat} \Rightarrow E_L = E_{mat} + v_{fib} (E_{fib} - E_{mat}) \quad \text{Eq. 2}^1$$

Just as strength was improved by fiber addition, stiffness is also improved, often by a great margin.

Micromechanically speaking, this reinforcement arises from the difference in stresses in the fiber and matrix. This generates shear stresses along the fiber-matrix interface, which transfers the load from the matrix to the fibers. In reality, the actual mechanical properties will deviate from these theoretical values if the fiber-matrix interface is damaged or disrupted. This can be due to fiber debonding, voids along the interface, or other defects. Thus, a strong fiber-matrix interface is critical to the performance of the composite.

## Epoxy Chemistry

Many PMCs use epoxy as their matrix material. This is because epoxies form a strong fiber-matrix interface, which is crucial, as explained earlier, to the performance of the resulting composite. This strong interface forms because epoxies are highly reactive, and readily bond to the surface of the glass fibers.

Epoxies are made from the reaction of an epoxide functional group and an amine group, creating a secondary amine and a secondary hydroxyl group (Figure 1).<sup>2</sup> This reaction occurs (ideally) at all ends of each molecule, with the resin component being the multifunctional epoxide (a molecule with multiple epoxide groups) and the hardener being a multifunctional amine.

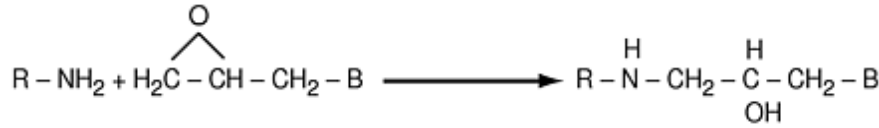


FIGURE 1: Reaction of a primary amine with an epoxide group to form a single molecule.<sup>2</sup>

In the case of reacting multifunctional components, the critical gelation point, the minimum percent of groups to react to transform the liquids into a network solid (or gel), can be calculated by

$$P_c = \frac{2}{f_{avg}}, \text{ where } f_{avg} = \frac{\sum N_i f_i}{\sum N_i} \text{ and } N_{epoxy} f_{epoxy} = N_{amine} f_{amine}^3$$

where  $f_{avg}$  is the average functionality (number of functional groups) of the mixture of resin and hardener,  $N_i$  is the number of moles of the component, and  $f_i$  is the functionality of the component.<sup>3</sup> As evidenced in these equations, a higher functionality in each component will cause the mixture to gel at a lower percent completion. However, this is balance by both cost and viscosity; as the functionality of a molecule increases, it begins to interact and “tangle” with its neighbors more (called steric hindrance), increasing viscosity. Therefore, a less expensive, lower viscosity resin and hardener are often chosen for most applications, including automobiles like Aptera's 2e.

Since the reaction of resin and hardener to form an epoxy is a chemical reaction, it is thermally

activated. The reaction is significantly sensitive to temperature; the ubiquitous rule of thumb is that every 10°C increase in temperature, the reaction rate constant increases by an order of magnitude, meaning the reaction will increase speed ten-fold. The reaction rate of a given reaction can be modeled by the Arrhenius equation, or

$$k = Ae^{-E/RT}$$

where k is the reaction rate constant, A is the collision frequency factor, E is the activation energy for the reaction, R is the universal gas constant, and T is the absolute temperature.

Also, since the reaction of an amine and an epoxide is exothermic, autoacceleration is possible. A rapid release of heat from the reaction cannot be dissipated by the system; this causes the temperature to rise, causing the rate constant to further increase. This will accelerate the process rapidly, sacrificing control over the process. However, the viscosity of the uncured resin-hardener mixture can also be modeled as an Arrhenius relationship with temperature.<sup>1</sup> autoacceleration would also reduce the viscosity, further accelerating the curing process.

Autoacceleration is a potential problem for resin curing, but a short curing time is also desired. In addition to influencing curing time, temperature also influences the crosslinking density of the resin. At higher temperatures, the resin and hardeners, which are both in the liquid state, will be less viscous. This will allow epoxide and amine groups to react on a more “even,” or isotropic, basis, creating more isotropic crosslinking, which will in turn improve the strength of the resin. This will also lead to a better interface with the fibers in a PMC. Thus, optimizing curing time and temperature can be a complex and sensitive process.

## **BROADER IMPACTS**

### *Health and Safety Issues*

As with all polymers, GFRPs have the potential to degrade over time when exposed to ultraviolet radiation, like sunlight. The two most significant problems that arise from this degradation are microcracking of the matrix (the epoxy), and weakening of the fiber-matrix interface. This weakening of the interface can lead to fiber pop-out.<sup>4</sup> Unless the car is designed against these two failure modes, the panel could fail catastrophically later in the car's life, possibly resulting in injury or death, broken body panels, road debris, or some other safety hazard.

Epoxy is often produced by step-growth polymerization from resin, a multifunctional polyepoxide, and a hardener, which is often a polyamine.<sup>5</sup> Both the resin and the hardener are in turn made from chemicals which are often toxic or dangerous, like bisphenol A, chlorinated hydrocarbons, and ammonia (in large doses). Therefore, potential health and safety risks exist. Also, the curing reaction itself is highly exothermic and gives off byproducts, and is therefore important to monitor as well. Thus, production of the epoxy matrix can be hazardous for the producers in the manufacturing of the matrix material and precursors from heat, chemicals, and byproducts.<sup>5</sup>

### *Manufacturability*

The matrix in PMCs, like epoxy in some GFRPs, is made in two steps: 1) polymerization, making an unsaturated, linear polymer that can be easily formed into the shape of the mold and will loosely hold the fibers, and 2) curing, which crosslinks the polymer into a network, which adheres to the fibers much better and has improved mechanical properties as a result.<sup>6</sup> The polymerization process is often made by the manufacturer of the precursor materials, and is therefore out of the control of the GFRP fabricator, like Aptera Motors. However, the curing step is done on site, and so it can be controlled and modified by the fabricator of the final product. This curing process has a profound effect on the final properties of the composite, and thus achieving properties within given design constraints can be a significant challenge if care is not taken. Thus, the status of various production variables must be continually assessed to ensure criteria are being met in production. The process must be developed with two critical stakeholders in mind. First, the producing company must design a process that is as cost effective as possible, usually meaning short cycle times while minimizing the cost of tooling. Second, the users require a GFRP panel that is sufficiently strong to be safe, while not being cost prohibitive.

### *Environmental Impact*

Although the use of GFRP panels increases the strength-to-weight ratio, and thus reduces the weight of the car, the matrix is still an organic polymer. Therefore, consumption of fossil fuels in its production, from supplying the organic matter to form the chemicals to providing fuel for the heating processes, is inevitable. Mitigation of this usage is still possible, however, and must be considered at all times. Therefore, an additional benefit of a stronger GFRP is the reduction of material used to fabricate the body panels of the cars, reducing

consumption of fossil fuels in its production. This in turn results in a less expensive car, which makes it more appealing to consumers. As electric cars, like Aptera Motors' 2e, displace conventional gasoline- and diesel-powered cars on the road, even fewer fossil fuels will be consumed, amplifying the benefit of the reduced weight of GFRPs. Another environmental concern arises from the production of the composite: all byproducts and chemicals must be disposed of or recycled, so this sector of production must be carefully monitored to reduce the impact to the environment. Effects on this third stakeholder, the environment and the biosphere, have a profound, albeit complicated impact on the first two stakeholders. Since this affects all three stakeholders significantly, it is critically important that the environmental effects be accounted for during the design and implementation of GFRP panels.

## **EXPERIMENTAL PROCEDURES**

In order to test the effects of cure temperature and IMPC temperature on the  $T_g$  and tensile strength of both resins, a testing matrix was designed, as shown in Table I. The middle level for both the cure temperature and IMPC temperature were chosen to approximate the manufacturers' specifications, then one additional level was chosen both above and below to determine if increasing or decreasing the cure or IMPC temperatures would affect the  $T_g$  or the tensile strength.

TABLE I: Testing Matrix for Analysis of Cure Schedule Effects on Properties of Resin A and Resin B

		IMPC Temperature		
		200°F	230°F	260°F
Cure Temperature	120°F			
	140°F			
	160°F			

For testing, the resin were mixed and prepared, in a repeatable and consistent fashion, and then prepared into samples at the time of use. Since the resins would cure, albeit a small amount, at room temperature, they were only prepared once for each batch of samples: each batch produced only one cure schedule with the appropriate number of replicates.

### ***Resin System A Preparation***

To prepare resin A for use in either the DSC or the Instron tensile tester, a 50 mL beaker was tared (on a mass-scale) and approximately 10 mL of the resin component was poured into the beaker. Then the mass of resin was measure (in g). This was used to calculate the mass of the hardener component needed, based on manufacturer's recommended mix ratio.

Next, another 50 mL beaker was tared, and the calculated amount of hardener was carefully measured out into the beaker. This hardener was then poured into the beaker containing the resin component into resin beaker and mix thoroughly by hand, as shown in Figure 2.

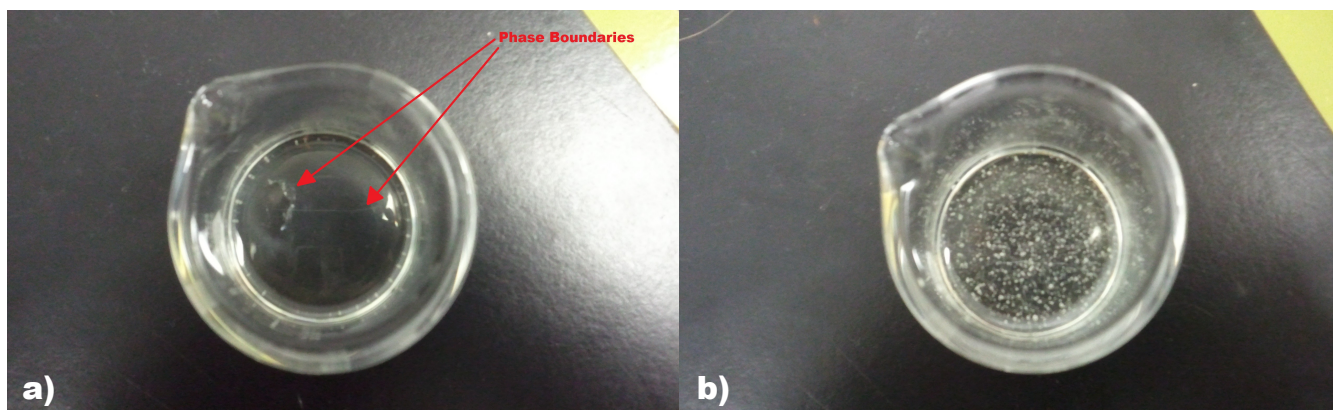


FIGURE 2: Resin A resin and hardener mixed together, showing phase boundaries, implying insufficient mixing in a) and complete mixing in b), evidenced by homogeneity and entrained air bubbles.

The glassware was cleaned immediately after dispensing in order to avoid requiring the used of concentrated acid or other harmful chemicals.

### *Resin System B Preparation*

Resin A was mixed in a similar fashion. First, as before, the resin component was poured into a 50 mL beaker. Since the manufacturer recommended ratio is on a weight-to-weight basis, rather than mass-to-mass as resin A was, the scale didn't need to be tared prior to pouring the resin. The volume of resin dispensed was then measured, and used to calculate the volume of hardener needed, based on the manufacturer's recommended mix ratio.

Next, the calculated amount of hardener was then carefully added to a 10 mL graduated cylinder. This amount of hardened was then added to the resin beaker, and mixed thoroughly by hand, just as before.

Finally, the glassware was cleaned immediately for the same reason as the resin A glassware.

### *DSC Test Preparation*

For DSC testing, each sample was created for only one batch of resin, made according to the appropriate procedure. Between 10 and 20 mg of mixed resin was dispensed, via a 5  $\mu$ L syringe, into the DSC sample pan. This sample pan was then inserted, alongside a reference pan, into the DSC. Next, the testing chamber was closed, and the testing scan, setup according to the testing matrix shown in Table I, was started. Just as in the sample preparation stage, the glassware was cleaned immediately.

To relate the properties of the resin to its structure, a useful metric is the percent cure of that sample. Since the curing of a two-part epoxy, like both resin A and resin B, is an exothermic process, an increase in the heat flow signal of the DSC will indicate curing. This can be used to determine the percent cure once compared to a standardized baseline cure schedule. An example of a typical curing exotherm can be seen in Figure3.

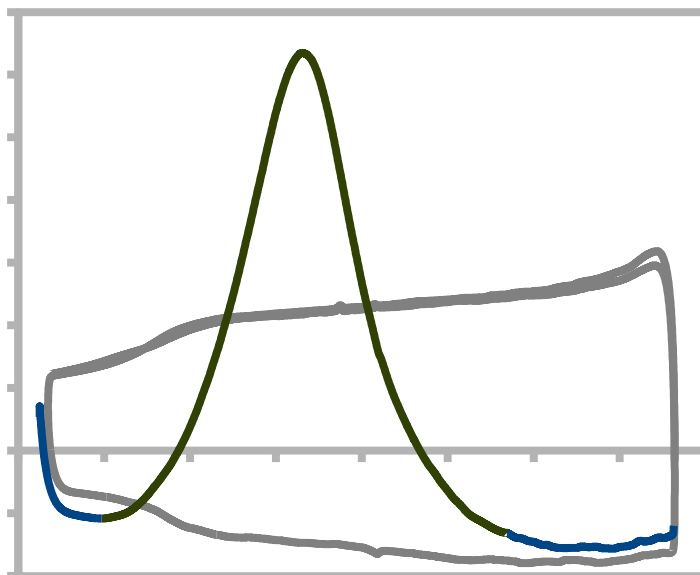


FIGURE 3: Typical DSC (differential heat flow vs. temperature) scan, showing the curing exotherm in green.

Another important measure of the thermal performance of a resin is the glass transition temperature. To determine the  $T_g$  from a DSC scan, The region of sudden drop in heat flow as a function of increasing temperature is used, and the inflection point of that region is the glass transition temperature temperature of that sample. A typical plot with the  $T_g$  region highlighted is shown in Figure 4.

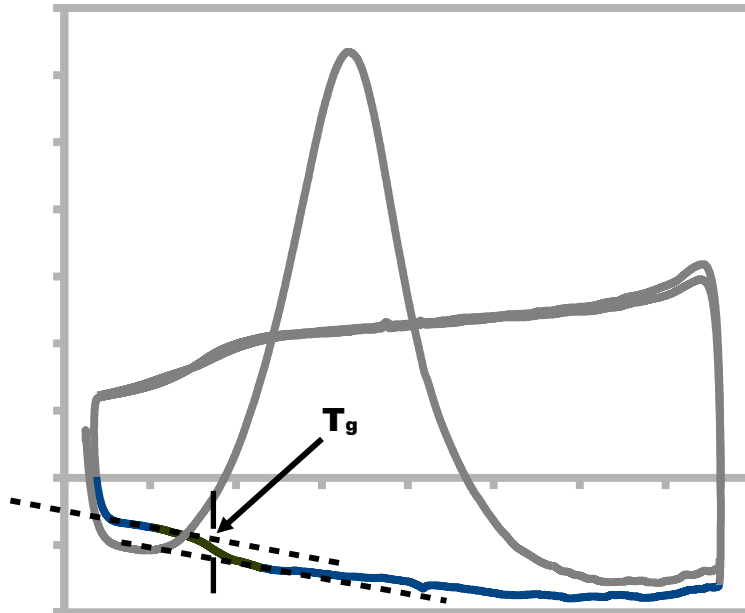


FIGURE 4: Typical DSC (differential heat flow vs. temperature) scan, displaying the tangential heat flow change on either side of the  $T_g$ , and the  $T_g$  itself.

### *Tensile Test Preparation*

In order to prepare the tensile testing samples, the resin to be used was first prepared as appropriate. Next the sample mold was coated in mold release, which in this case was a commercial silicone lubricant. Then the resin was further mixed and degassed for 5 min in a demixer, as pictured in Figure 5.



FIGURE 5: Demixer used to further prepare the resin for use in the producing tensile samples.

Next, the mixed and degassed resin was poured into the 3 mold cavities in sample mold, as shown in Figure 6, and the excess resin was removed by scraping off.



FIGURE 6: Mixed and Degassed resin being poured into tensile sample mold.

The sample mold was then placed in a preheated (to the cure temperature of the batch) low-temperature oven and cured for the manufacturer's recommended duration. Then, the temperature was set to the batch's IMPC temperature. The oven was then allowed to reach the IMPC temperature, and then post-cure for the specified time.

Once the samples were cured, the samples were carefully removed from the mold and labeled for testing.



## RESULTS

### DSC Analysis

In order to assess the degree of cure for the resin for each cure schedule, a baseline cure schedule must be performed. In order to do this, the resin is heated from room temperature to 250°C (482°F) at a rate of 10°C/min (18°F/min), then cooled back to room temperature at the same rate. This process was then repeated. This baseline cure schedule gives off a clear exothermic peak; integrating this peak yields the energy (per unit mass) that is given off by a fully cured sample, as shown in Figure 7.

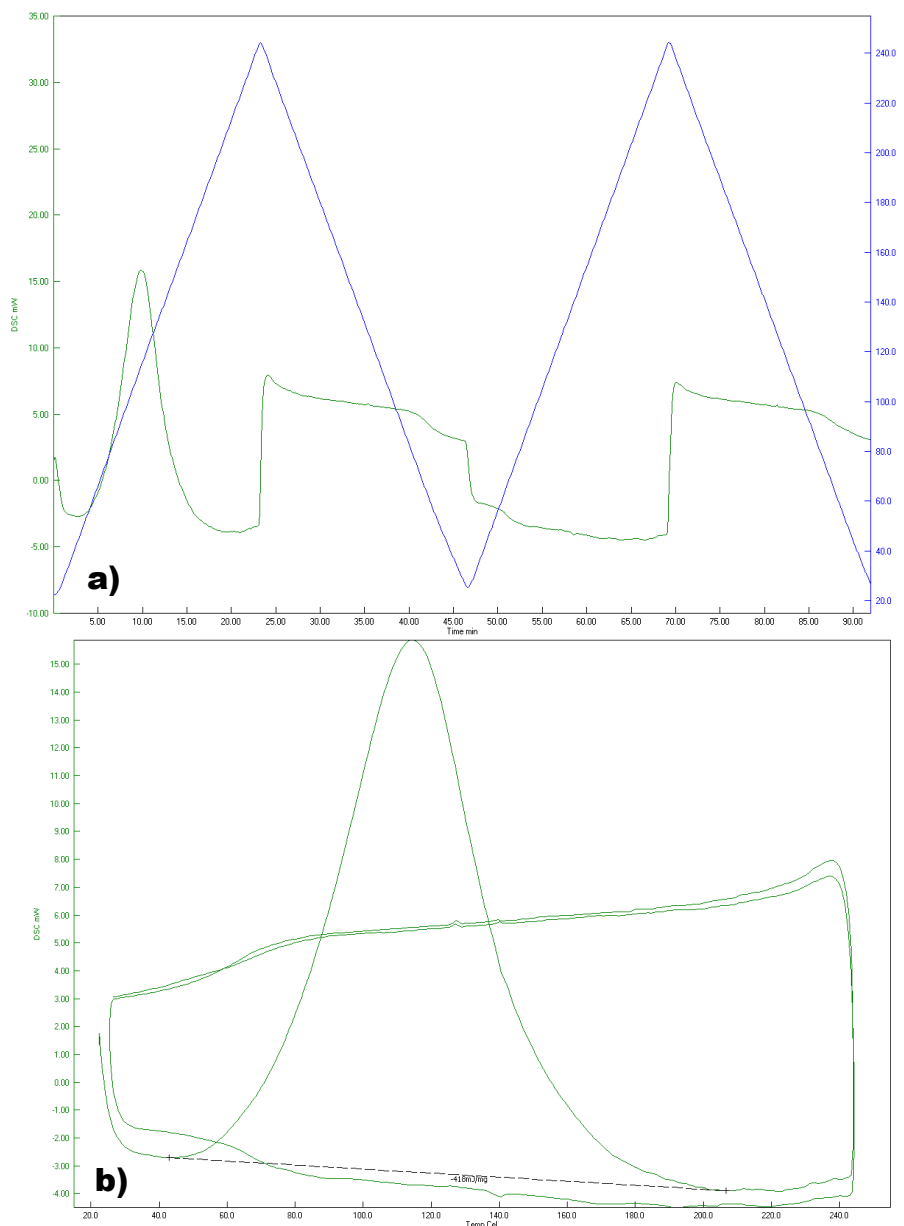


FIGURE 7: Baseline cure schedule for Resin A, showing heat flow change in green for both plots, the temperature rate of change in blue (a), and the area under the curve, representing the energy given off per unit mass (b).

After determining the amount of energy given off by fully curing the resin (via a baseline cure), each cure schedule was performed, utilizing a ramp rate from room temperature to the curing temperature, curing temperature to IMPC temperature, and IMPC temperature back to room temperature of 16°C/min (28.8°F/min). The faster rate of temperature change was used to better simulate actual processing conditions than the 10°C/min for the baseline cure. Once this was completed, each cure schedule was assessed by determining the area under the curing exotherm. This area represents the heat given off during curing, and is used to calculate the percent cure with the equation

$$\alpha_C = \frac{H}{H_F} \quad ^1$$

where  $\alpha_C$  is the degree of cure (in decimal percent),  $H$  is the heat given off during the cure schedule, and  $H_F$  is the heat given off during the baseline cure.

For the second piece of thermal analysis, the same DSC scan was analyzed. The loss of heat capacity, represented by a decrease in the heat flow signal (Figure 8), displays the glass transition temperature ( $T_g$ ) of the resin. The middle of the  $T_g$ , equivalent to the inflection point of the curve, was used in the analysis of the different resins.

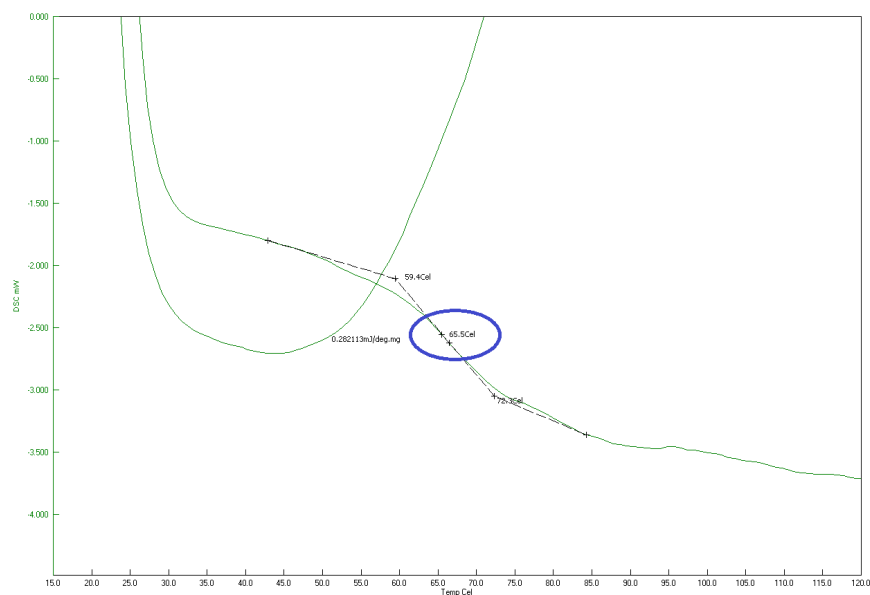


FIGURE 8: DSC baseline cure showing region for determining the  $T_g$ . The  $T_g$  at the inflection point was used to determine the  $T_g$  of the scan.

Using these techniques, each of the samples, regardless of cure schedule, were determined to be fully cured, so no quantitative comparison of the degree of cure between samples was necessary.

To verify that all samples were in fact fully cured, at least one validation test was performed for each resin system. Using the lowest curing temperature, the lowest IMPC temperature that produced near-full curing was selected. The resulting DSC scans for each resin system can be seen in Figure 9.

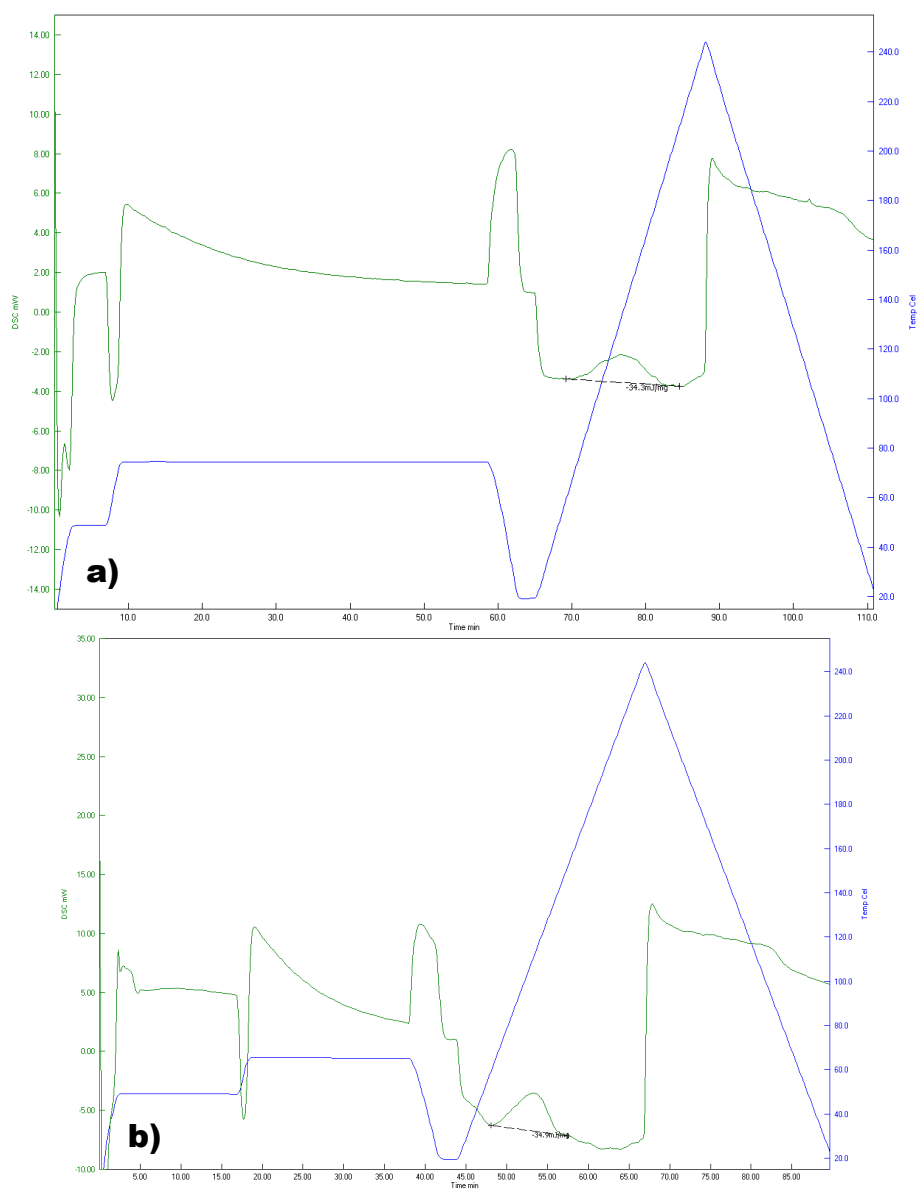


FIGURE 9: DSC test validation scans, including labeled curing integrations, of Resin A (a) and Resin B (b). The corresponding IMPC temperatures are 167°F and 150°F, respectively.

Using these IMPC temperatures, resin A was 91.8% cured and resin B was 92.1% cured. Since these validating temperatures are more than 30°F lower than the lowest IMPC temperature in the testing matrix, it is to be expected that all samples are fully cured.

However, the analysis of the glass transition temperatures yielded reasonable results, as shown in Table II and Table III. The mean  $T_g$  for resin A was 154.5°F, while the  $T_g$  for resin B was 164.4°F.

TABLE II: Glass Transition Temperatures (°F) of Resin A For Different Cure Schedules

Resin A		IMPC Temperature		
		200°F	230°F	260°F
Cure Temperature	120°F	---	147.92	168.98
	140°F	149.72	156.74	167.90
	160°F	---	128.84	161.06
Standard Deviation:		13.92°F		

TABLE III: Glass Transition Temperatures (°F) of Resin B For Different Cure Schedules

Resin B		IMPC Temperature		
		200°F	230°F	260°F
Cure Temperature	120°F	---	186.44	118.04
	140°F	173.66	171.32	158.90
	160°F	---	174.20	168.08
Standard Deviation:		22.02°F		

Unfortunately, none of the cure schedules utilizing a 200°F in-mold post-cure (IMPC) produced discernible  $T_g$  values. One-way ANOVAs were then used to determine if either the cure temperature or the IMPC temperature have a statistically significant effect on the  $T_g$  of either resin system A or resin system B, the results of which are tabulated in Table IV. Full results can be found in Appendix A.

TABLE IV: One-way ANOVA Results for Determining Statistical Significance of Cure or IMPC Temperature on  $T_g$ 

One-way ANOVA	Std Dev (°F)	P-value
Tg resin A vs. Cure Temperature	15.07	0.612
Tg resin A vs. IMPC Temperature	10.53	0.146
Tg resin B vs. Cure Temperature	24.92	0.729
Tg resin B vs. IMPC Temperature	19.67	0.283

Since all ANOVAs produced p-values above 0.05, neither the cure temperature nor the IMPC temperature has a statistically significant effect on either resin system.

In order to determine the necessary sample sizes for each of the ANOVAs used in analyzing the effect of cure schedule on the glass transition temperature of the resins, power and sample size analysis was used. The difference between the highest and lowest mean  $T_g$  was used from each ANOVA, and a confidence interval of 95% was chosen for the target power. The resulting sample sizes needed are tabulated in Table V.

TABLE V: Number of Samples Needed For Statistical Significance of Cure Schedule Effect On  $T_g$ 

One-way ANOVA	Std Dev (°F)	$T_{g,max} - T_{g,min}$	# Samples
Tg resin A vs. Cure Temperature	15.07	13.5°F	40
Tg resin A vs. IMPC Temperature	10.53	21.48°F	9
Tg resin B vs. Cure Temperature	24.92	18.9°F	55
Tg resin B vs. IMPC Temperature	19.67	28.98°F	16

Therefore, a sample size of at least 55 would be needed to observe all differences in glass transition temperatures as statistically significant. Since this is a much larger population than used, it is unlikely that statistical significance would be observed. If 5 samples for each cure schedule were used, equating to a sample size of 15, the IMPC temperature is likely to have an effect on the glass transition temperature of resin A, and an effect of IMPC temperature on the glass transition temperature of resin B might be observed if the standard deviation decreases. A sample size of 15, which is more realistic than 55, is therefore likely to show statistical significance.

### Tensile Test Analysis

The tensile samples were prepared, using the same cure schedules as the DSC scans, then clearly labeled for testing (Figure 10).

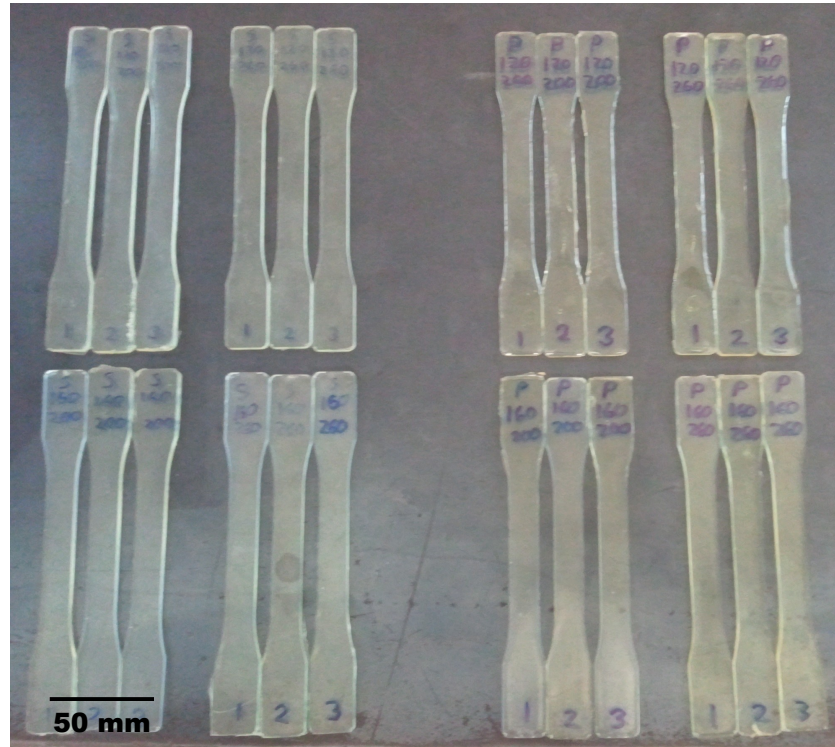


FIGURE 10: Tensile testing samples, showing geometry and designations.

Next, the samples were inserted in the the Instron tensile testing machine, and a testing method was established for determining the tensile strength of each sample from the test geometry and the maximum load on the sample. This method was repeated for all samples, and produced the data shown in Table IV and Table VII, and shown graphically via box plot in Figure 11. The average tensile strengths for the resins were determined to be 60.44 MPa and 63.19 MPa, respectively.

TABLE VI: Tensile Strength (MPa) for Each Resin A Sample as a Function of Cure Temperature and IMPC Temperature

Resin A		IMPC Temperature			
		200°F		260°F	
		Sample	Average	Sample	Average
Cure Temperature	120°F	61.91	59.28	59.46	60.52
		58.88		61.15	
		57.04		60.95	
	160°F	61.93	61.11	57.04	60.83
		60.73		65.99	
		60.67		59.47	
Standard Deviation:		2.40 MPa			

TABLE VII: Tensile Strength (MPa) for Each Resin B Sample as a Function of Cure Temperature and IMPC Temperature

Resin B		IMPC Temperature			
		200°F		260°F	
		Sample	Average	Sample	Average
Cure Temperature	120°F	69.65	68.50	64.71	63.85
		68.62		61.41	
		67.25		65.41	
	160°F	62.16	55.29	67.04	65.10
		53.54		63.81	
		50.17		64.46	
Standard Deviation:		5.87 MPa			

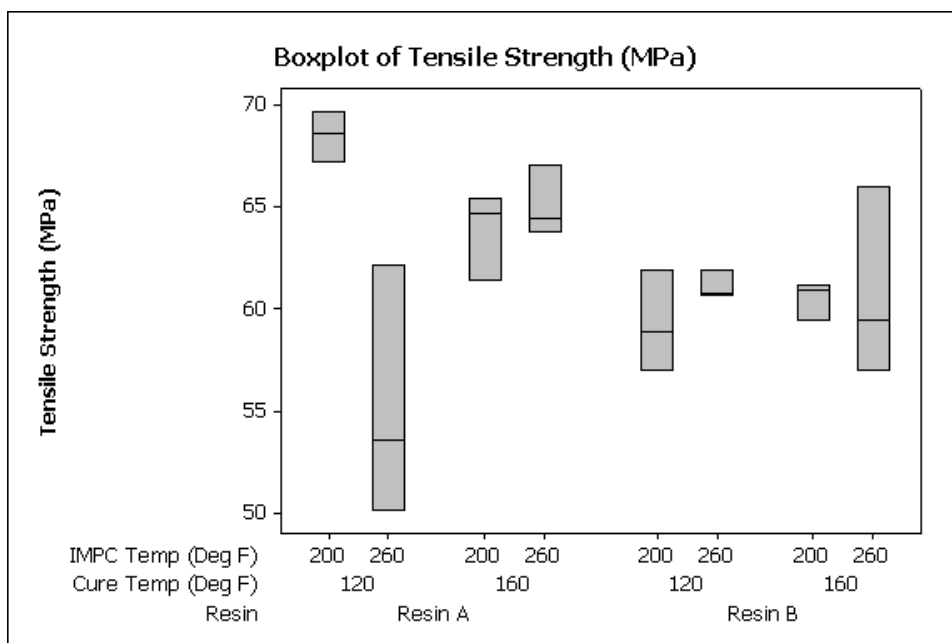


FIGURE 11: Box plot showing tensile strength as a function of resin system, cure temperature, and IMPC temperature.

In order to analyze the data, one-way ANOVAs were again utilized, as shown in Table VIII.

TABLE VIII: One-way ANOVA Results for Determining Statistical Significance of Cure or IMPC Temperature on Tensile Strength

One-way ANOVA	Std Dev (MPa)	P-value
Tg resin A vs. Cure Temperature	2.51	0.746
Tg resin A vs. IMPC Temperature	2.45	0.466
Tg resin B vs. Cure Temperature	5.99	0.473
Tg resin B vs. IMPC Temperature	5.21	0.075

As shown by the p-values for each of the ANOVAs, neither the cure temperature nor the IMPC temperature have a statistically significant effect on the tensile strength of either resin system.

As before, power and sample size analysis was used to determine the sample size necessary to observe statistical significance. These results are tabulated in Table IX.

TABLE IX: Number of Samples Needed For Statistical Significance of Cure Schedule Effect On Tensile Strength

One-way ANOVA	Std Dev (MPa)	TS <sub>max</sub> - TS <sub>min</sub>	# Samples
Tensile Str resin A vs. Cure Temperature	2.51	0.48 MPa	844
Tensile Str resin A vs. IMPC Temperature	2.45	1.07 MPa	164
Tensile Str resin B vs. Cure Temperature	5.99	2.58 MPa	168
Tensile Str resin B vs. IMPC Temperature	5.21	5.98 MPa	25

Due to small standard deviations and small differences in means, a sample size of 844 would be needed to observe statistical significance in the effect of cure temperature and IMPC temperature on tensile strength of both resin systems with a confidence interval of 95%. If 15 samples were used for each of the cure schedules tested, a sample size of 30 would be produced, and even for this reasonable sample size, only the effect of IMPC temperature on the tensile strength of resin B would be likely to be statistically significant. Therefore, it is likely only the effect of IMPC temperature on resin system B will be statistically significant, even at relatively large sample sizes.



## DISCUSSION

As shown, neither the glass transition temperature nor the tensile strength was affected by the cure or IMPC temperatures within the ranges of testing. This could be explained by observing the DSC scans for the different cure schedules. Many of the resins showed an exotherm, indicative of curing in thermoset resins, prior to the second half of the IMPC stage of the curing schedule, like the scan shown in Figure 12. This suggests that the efficacy of either step of the process is not significantly affected by the temperature of that process.

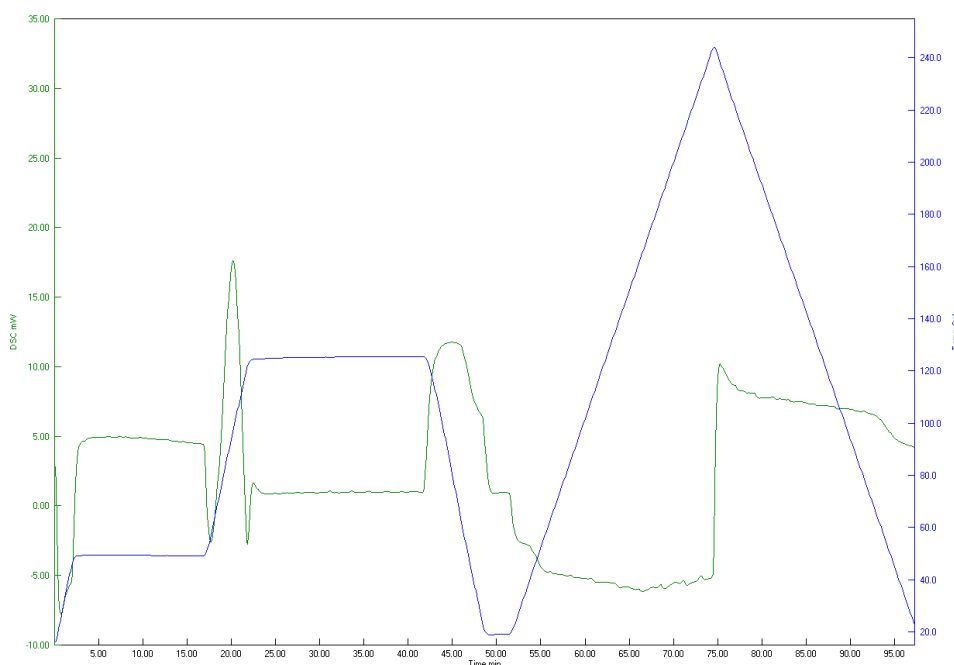


FIGURE 12: DSC cure schedule for resin system B, with a 120°F cure temperature and 260°F IMPC temperature. The heat flow curve (in green) shows a curing exotherm between the cure and IMPC steps, at about 20 minutes.

This could also explain why a significant difference was observed in the resin B samples. Both the  $T_g$  and the tensile strength as a function of cure temperature showed a large standard deviation among the samples, as displayed in Table IV and Table VIII respectively. However, the IMPC samples for both analyses showed lower standard deviations, and significantly lower p-values for the one-way ANOVAs as a result. It would appear, therefore, that temperature has a much more significant effect during the curing step than the post-curing step.

This in turn means that the reaction of the epoxide groups in the resin and the amine groups in the hardener are not affected, at least primarily, by moderate changes (20°F for the cure temperature and 30°F for the IMPC temperature) in the temperature. It would seem, therefore, that other effects on the reaction rate of the resin and hardener, like viscosity or geometric reaction conditions (size of the reaction vessel, etc.), outweigh or nullify the effects of temperature on the reaction rate, and thus the  $T_g$  and tensile strength of the resulting resin. The larger variation in  $T_g$  and tensile strength as a function of temperature during the curing step than the IMPC

step for resin B could be due to the exponential effect temperature has on the reaction rate constant and the viscosity of the uncured resin. During the curing step, the resin begins uncured, so the reaction of a polyepoxide resin molecule and a polyamine hardener molecule is a function of both the molecules moving through the uncured resin (viscosity) and interacting favorably once they are in close proximity (reaction rate constant), the reaction of the two molecules is sensitive to temperature. Conversely, during the post-curing step, the resin is already mostly cured, so the viscosity is virtually infinite. Therefore, only the reaction rate constant is truly affected by temperature, and even then only affects very few molecules that are already in close proximity to one another immediately after the curing step. This would lead to a significantly diminished effect of temperature on the resin, and thus the properties that result. This is reinforced by the standard deviations and the p-values for the one-way ANOVAs as a function of IMPC temperature for resin B being significantly lower than those that are a function of cure temperature.

Since these observations are a result of testing and statistics, increasing the number of replicates during testing, especially the DSC testing (since no replicates were tested), could lead to more conclusive results. Since increasing replication would reduce variation in the data, statistical significance would become more likely. This could allow for the observation of changes in either the  $T_g$  or the tensile strength of either resin system.

## CONCLUSIONS

1. The effects of cure temperature and IMPC temperature on the glass transition temperature and the tensile strength of both resin A and resin B are not statistically significant.
2. The mean  $T_g$  for resin A was 154.5°F with a standard deviation of 13.9°F, while the mean  $T_g$  for resin B was 164.4°F with a standard deviation of 22.0°F.
3. The average tensile strength of the resin A samples was 60.44 MPa with a standard deviation of 2.40 MPa, and the average tensile strength of the resin B samples was 63.19 MPa with a standard deviation of 5.87 MPa.
4. More statistically significant results of the effect of cure schedule on the  $T_g$  of both resin A and resin B might be observed if 5 replicates per cure schedule were performed, resulting in a sample size of 15.
5. It is unlikely further tensile testing will show statistical significance for the effect of curing schedule on tensile strength either resin, even with a sample size of 30, equivalent to 15 replicates.
6. Since the cure schedule has no statistically significant effect on either the  $T_g$  or the tensile strength of resin A or resin B, a cure schedule should be chosen to minimize both cost (lower temperature) and minimize processing time.

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## APPENDICES

### Appendix A: One-way ANOVAs for Analyzing Statistical Significance of Testing Results

One-way ANOVA: Tg Resin A (Deg F) versus Cure Temp (Deg F)						One-way ANOVA: Tg Resin A (Deg F) versus IMPC Temp (Deg F)					
Source	DF	SS	MS	F	P	Source	DF	SS	MS	F	P
Cure Temp (Deg F)	2	253	126	0.56	0.612	IMPC Temp (Deg F)	2	718	359	3.24	0.146
Error	4	909	227			Error	4	444	111		
Total	6	1162				Total	6	1162			
S = 15.07 R-Sq = 21.77% R-Sq(adj) = 0.00%						S = 10.53 R-Sq = 61.82% R-Sq(adj) = 42.72%					
Individual 95% CIs For Mean Based on Pooled StDev						Individual 95% CIs For Mean Based on Pooled StDev					
Level	N	Mean	StDev			Level	N	Mean	StDev		
120	2	158.45	14.89	(------*-----)		200	1	149.72	*	(------*-----)	
140	3	158.12	9.17	(-----*-----)		230	3	144.50	14.26	(-----*-----)	
160	2	144.95	22.78	(------*-----)		260	3	165.98	4.29	(------*-----)	
120 140 160 180						128 144 160 176					
Pooled StDev = 15.07						Pooled StDev = 10.53					
One-way ANOVA: Tg Resin B (Deg F) versus Cure Temp (Deg F)						One-way ANOVA: Tg Resin B (Deg F) versus IMPC Temp (Deg F)					
Source	DF	SS	MS	F	P	Source	DF	SS	MS	F	P
Cure Temp (Deg F)	2	425	212	0.34	0.729	IMPC Temp (Deg F)	2	1360	680	1.76	0.283
Error	4	2484	621			Error	4	1548	387		
Total	6	2908				Total	6	2908			
S = 24.92 R-Sq = 14.60% R-Sq(adj) = 0.00%						S = 19.67 R-Sq = 46.77% R-Sq(adj) = 20.16%					
Individual 95% CIs For Mean Based on Pooled StDev						Individual 95% CIs For Mean Based on Pooled StDev					
Level	N	Mean	StDev			Level	N	Mean	StDev		
120	2	152.24	48.37	(------*-----)		200	1	173.66	*	(------*-----)	
140	3	167.96	7.93	(-----*-----)		230	3	177.32	8.03	(-----*-----)	
160	2	171.14	4.33	(-----*-----)		260	3	148.34	26.64	(------*-----)	
120 150 180 210						120 150 180 210					
Pooled StDev = 24.92						Pooled StDev = 19.67					
One-way ANOVA: Tensile Str Resin A (MPa) versus Cure Temp (Deg F)						One-way ANOVA: Tensile Str Resin A (MPa) versus IMPC Temp (Deg F)					
Source	DF	SS	MS	F	P	Source	DF	SS	MS	F	P
cure	1	0.70	0.70	0.11	0.746	IMPC	1	3.45	3.45	0.57	0.466
Error	10	62.86	6.29			Error	10	60.11	6.01		
Total	11	63.56				Total	11	63.56			
S = 2.507 R-Sq = 1.10% R-Sq(adj) = 0.00%						S = 2.452 R-Sq = 5.43% R-Sq(adj) = 0.00%					
Individual 95% CIs For Mean Based on Pooled StDev						Individual 95% CIs For Mean Based on Pooled StDev					
Level	N	Mean	StDev			Level	N	Mean	StDev		
120	6	60.194	1.907	(------*-----)		200	6	59.899	1.797	(------*-----)	
160	6	60.676	2.989	(-----*-----)		260	6	60.972	2.965	(-----*-----)	
58.5 60.0 61.5 63.0						58.5 60.0 61.5 63.0					
Pooled StDev = 2.507						Pooled StDev = 2.452					
One-way ANOVA: Tensile Str Resin B (Deg F) versus Cure Temp (Deg F)						One-way ANOVA: Tensile Str Resin B (Deg F) versus IMPC Temp (Deg F)					
Source	DF	SS	MS	F	P	Source	DF	SS	MS	F	P
cure	1	19.9	19.9	0.56	0.473	IMPC	1	107.3	107.3	3.95	0.075
Error	10	358.7	35.9			Error	10	271.4	27.1		
Total	11	378.7				Total	11	378.7			
S = 5.989 R-Sq = 5.27% R-Sq(adj) = 0.00%						S = 5.210 R-Sq = 28.33% R-Sq(adj) = 21.16%					
Individual 95% CIs For Mean Based on Pooled StDev						Individual 95% CIs For Mean Based on Pooled StDev					
Level	N	Mean	StDev			Level	N	Mean	StDev		
120	6	61.896	8.263	(------*-----)		200	6	66.175	2.986	(-----*-----)	
160	6	64.475	1.863	(-----*-----)		260	6	60.196	6.735	(-----*-----)	
59.5 63.0 66.5 70.0						56.0 60.0 64.0 68.0					
Pooled StDev = 5.989						Pooled StDev = 5.210					