OPTIMIZATION OF CURE CYCLES USING AN ESR (ENCAPSULATED SAMPLE RHEOMETER)

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ABSTRACT

One of the most critical steps in the production of composite material product is the cure cycle. The recommended cure cycles are usually provided by the prepreg suppliers. These cycles are often adjusted by trial and error until optimum final product properties are achieved. Operating an autoclave or oven while simultaneously measuring material properties can prove difficult due to size and cost restraints. The introduction of the ESR (encapsulated sample rheometer), which meets the ASTM 7750, has provided a cost-effective method to cure composite materials under any cure cycle necessary. In addition, the ESR is capable of measuring gel, cure, and final physical properties from those conditions [1].

This paper evaluates simulated cure cycles with varying temperature ramps and hold temperatures, time at temperature, and the application of pressure while measuring the inherent cure properties of several resin and fiber packages. These simulations lead to the conditions for the optimum full cure. Next, the physical properties were measured and compared at the same temperature to determine the impact of cure conditions on the final product. Comparison of physical properties and Tg leads to optimization of the process, thus balancing efficiency and ensuring reliable material properties.

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INTRODUCTION

The measurement of cure in a thermoset polymer matrix composite which produces a very high modulus laminate is difficult. Many different techniques have been developed to measure cure in such systems. Methods used for prepreg include measurement of thermal properties during cure with a Differential Scanning Calorimeter (DSC) that measures heat of reaction during cure of the matrix. DSC can be used to determine activation energies via Kissinger's method.[2] however, it can be difficult to model the kinetic impact of multiple layers using this method. Thermal Mechanical Analysis (TMA) of cured laminates is another method commonly used to determine state of cure and glass transition temperature of prepregs.[3] Newer alternative methods include measurement of the change in electrical properties of the matrix during cure such as dielectric properties, and change in sound transmission such as ultrasonic techniques.[4]

The original ASTM method for measuring the gel point on prepregs is described in D3532 (Standard Test Method for Gel Time of Carbon Fiber-Epoxy Prepreg).[5] It has been the legacy standard for the past fifty years. Recently, the introduction of ASTM D7750 [6] has expanded the capabilities available for measuring gel and cure. This approach has been developed to use viscoelastic properties measured after the application of a small mechanical strain. There are a variety of mathematical models used to describe such reactions using either DSC or mechanical data. A popular simple model [6] is shown in Equation 1:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n \qquad \text{Equation 1}$$

Where α is the degree of cure, t is time, k is the rate constant and n is the order of the reaction. The solution to this equation when n=1 is given by Equation 2:

$$\ln(1-\alpha) = \ln A - k(t-t_i) \qquad \text{Equation 2}$$

the value of (1- α) represents the unreacted material, A is a constant, k is the rate constant, t is time and t_i is the time at which the reaction is initiated. The slope in the plot of ln(1- α) versus t is the rate constant at the test temperature and the x-intercept is the t_i. The rate constant k often has a dependence on temperature. The rate constant k should increase as the test temperature increases. The rate constant often follows the Arrhenius Model as a function of temperature:

$$k = Ae^{-Ea/RT} \qquad \text{Equation 3}$$

Where k is the Rate Constant, A is the pre-exponential factor, E_a is the Energy of Activation, R is the Universal gas constant and T is the Temperature (1/K).

Taking the natural log of each side of Equation 3 gives Equation 4:

$$\ln k = \ln A - (E_a/RT) \qquad \text{Equation 4}$$

The slope in the plot of ln k and 1/T is equal to E_a/R.

This study looked at the application of these models to the actual measurement of the cure reaction by mechanical changes in the prepreg during cure. There have been several resin studies using similar models based on viscosity.[6] The expectation in this study was that the addition of fibers in a prepreg should have minimal effect on the cure kinetics compared to neat resins.

The studies in this paper look at the cure reaction in the prepreg without removing the resin from the prepreg and using multiple layers of prepreg that result in a coupon that simulates the manufacture of a part.

Recent improvements in this system have also allowed a thorough characterization of the state of cure by the measurement of Tg.

DESCRIPTION OF THE APPARATUS

The instrument is a commercially available DMA called the ESR (Figure 1).

Figure 1. The Encapsulated Specimen Rheometer (ESR).

The system has two parallel plate dies (Figure 2). The die surface is grooved to help hold high modulus samples and prevent slippage.

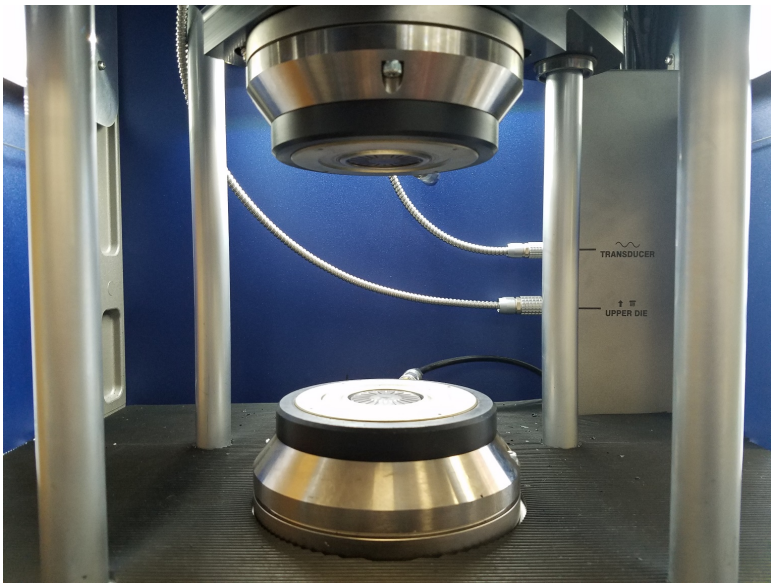

Figure 2. Closeup of instrument dies.

The outer edge of the sample cavity contains two seal plates and two seals, which completely seal the sample cavity when the dies are closed. The sample is placed onto the lower die and then the upper die is brought down. An o-ring in the sample chamber prevents the escape of resin to maintain a consistent fiber / resin ratio and helps build the pressure in the cavity to limit voids, prevent slippage and thus improve the repeatability of the test. The upper die is attached to a torque transducer. This placement of the transducer eliminates the measurement of lower die seal and bearing frictions. A cure test is typically run continuously with a strain of 0.7% and an oscillation frequency of 1 Hz or 1.667 Hz. The die dimensions, sample thickness, frequency of oscillation and strain are all used with appropriate rheological equations to convert torque to shear modulus. A Fourier Transform of the data separates the torque signal into an elastic and a viscous or loss component. This torque signal is then converted to viscoelastic properties of the material under test: elastic shear modulus G', loss shear modulus G", complex shear modulus G*, and Tan(Delta) [=G"/G'].

The digitally controlled thermal system allows the measurement of material properties from room temperature to 350 °C. The temperature can be ramped upwards from very low rates of 0.2 °C /minute to a very rapid rate of 50 °C/minute. A forced air cooling system allows the temperature to be reduced at rates of up to 30 °C/minute. The rapid response to temperature changes also enables the system to follow the temperature changes in most production systems and enables a more accurate estimation of the true state of the material during any cure profile.

Figure 3 shows a sample after processing with a cure profile. The o-ring is visible at the outer diameter and the sample is contained within two layers of film for ease of removal.

Figure 3. Prepreg sample after processing with a temperature profile

VISCOELASTIC PROPERTIES OF POLYMERS

In practical terms, the process of manufacturing composites is to form (layup) the prepreg to the surface of the tool while in a predominately viscous state and capture the resin by various bleeder, breather and barrier films. It is important create a test specimen that contains multiple layers and resembles a part created by a layup. The changes in the viscoelastic properties during processing are illustrated in Figure 4. While in the low viscosity (viscous) state, gases are removed, and voids are compressed. This is followed by an increase in modulus (cure) until the material is solid (elastic) and retains the shape that is required in a structure. As noted above, layup, degassing and consolidation occur while the material is in the predominately liquid state as measured by a low value of the storage modulus G', a relatively large value for the loss modulus (*G*") and a relatively large value of Tan(Delta) [=G"/G']. The final cure stage is measured by achieving the appropriate final storage modulus (*G*') at the required temperature. Conceptually G' can be considered a measure of how solid (elastic) the material is while G" is a measure of its viscosity. While this is not an entirely accurate description of G' and G", it is empirically useful. *G*', *G*" and Tan(Delta) provide tools for monitoring the transition of the prepreg from a 'liquid' prepreg to a solid state laminate. These parameters are, in fact, the technical basis for tests that support current design limits.[7] Existing specifications for flow, tack, drape, gel time, cure time and glass transition temperatures are all measures of viscoelastic state; however, they are difficult to quantify in real time by legacy-specified methods and cannot be incorporated as triggers for automated processing.

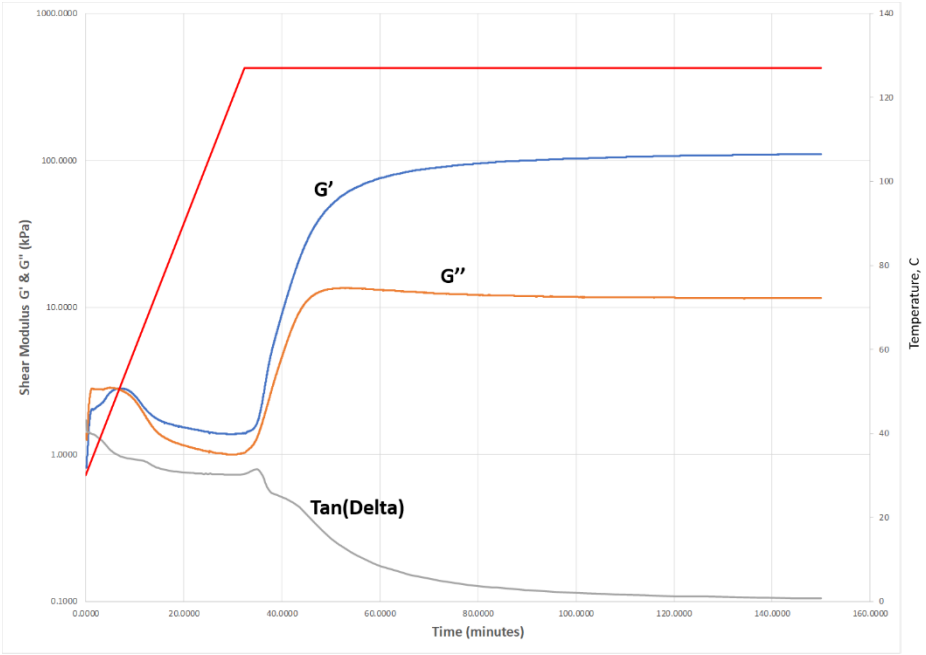

Figure 4. An example of the changes in viscoelastic properties that occur during the processing of a prepreg. The applied temperature profile is also shown.

Understanding the viscoelastic properties allows for a better assessment of the current state of the material for informed decisions regarding quality, processability and any possible changes to processing conditions.

For those not familiar with the complex shear modulus (G^*), it is sufficient to think of it as the force required to change the shape of a prepreg. This can be further divided into the force required for a temporary change in shape (elastic modulus G') where the material will 'snap back' after the force is removed and the force that is converted to heat within the material (loss modulus G''). A term used to evaluate the liquid versus solid character of the material including the ability to recover its shape is the Tan(Delta) which is equal to the flow characteristic divided by the elastic characteristic. The Tan(Delta) value can indicate the ability of the resin to flow. When the value is greater than 0.500, then the material can flow and allow the prepreg layup to change its shape during processing. When the value is less than 0.300, then the material will resist changes in its shape. After cure, the Tan(Delta) value often is significantly lower than 0.100 and the prepreg is now very stiff and will not change its shape unless the temperature is raised above its Tg. The Tan(Delta) peak observed near the gel point is also a useful point that is repeatable and occurs in the region that has the empirical definition of gel. The important point is that for a given fiber/resin combination the data is quantitative, repeatable and informative with respect to the material state.

In addition to measuring the state of cure using mechanical properties, the final state of cure using Tg of a sample after cure. The Tg value is determined by either the peak in G", the peak in Tan(Delta) or the knee in the G' / G* curves.

EXPERIMENTAL

Materials

1. Prepreg No. 1
2. Prepreg No. 2
3. Unidirectional Tape

Test Conditions

The tests used in these studies are described below:

1. Processing Conditions: Most prepregs are processed by ramping the temperature from room temperature up to the hold temperature. After leaving the prepreg at the hold temperature for a sufficient time to finish the thermoset reaction, the temperature is reduced back to room temperature. This portion of the study determined the effect of the hold temperature on the final cure state. It also determined the effect of ramp rate on the final cure state.
    a. Ramp at 3 C/minute and hold at 117 °C for 2 hours
    b. Ramp at 3 °C/minute and hold at 107 °C for 2 hours
    c. Ramp at 3 °C/minute and hold at 127 °C for 2 hours
    d. Ramp at 1 °C/minute and hold at 127 °C for 2 hours
2. Isothermal Processing: The introduction of the ESR has allowed the testing of prepregs under isothermal processing. The purpose for the isothermal testing is to apply the results at 2 or more temperatures to reaction models in order to predict the processing of prepregs under non-isothermal conditions or other isothermal temperatures. The prepregs in this study were tested at 107 °C, 117 °C, 127 °C, 137 °C and 147 °C. The unidirectional tape was tested at 167 °C, 177 °C and 187 °C.

RESULTS

Non-isothermal Studies

Figure 5 shows the cure of Prepreg No. 1 under three different processing conditions. All the temperature profiles used a ramp of 3 °C/minute, but each had a different hold temperature. As expected, the higher temperature generally cured faster. However, the higher hold temperature also showed a reduction in the G' value at the hold temperature. The Tg values from these tests are given in Table 1. The Tg value from all three hold temperatures varied only slightly or up to 4 C over a range of 20 °C in the hold temperature.

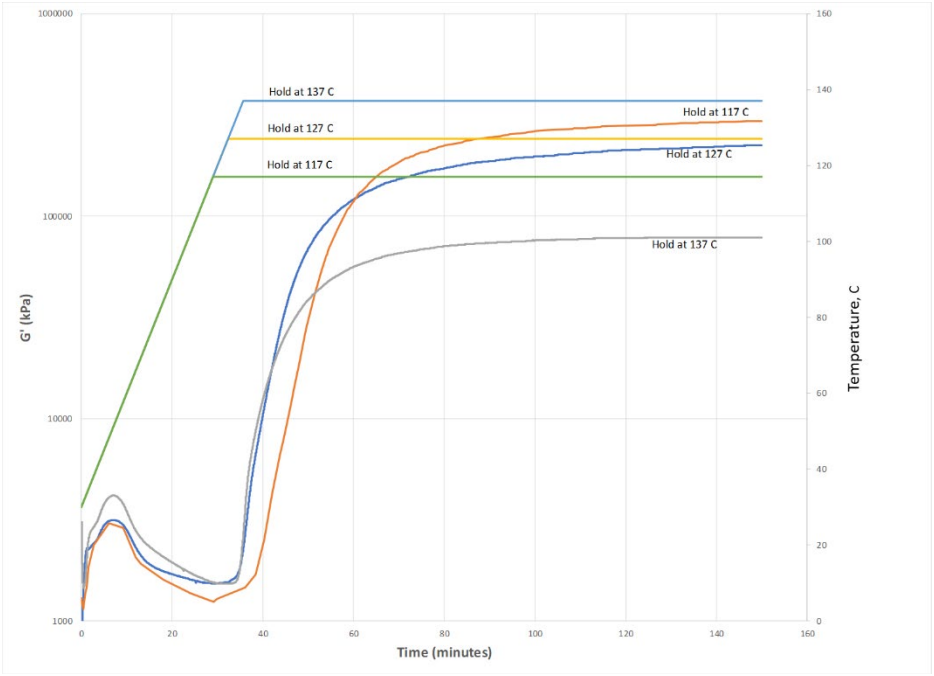

Figure 5. Changes in the elastic shear modulus G' during the processing of a prepreg with three different hold temperatures. Higher temperatures speed up the processing and reduce the final G' value at the hold temperature.

Figure 6 shows the G' results from one hold temperature but with two different ramp rates using Prepreg No. 1. The cure curve gel point with the slower ramp is shifted to a longer time as expected. The Tg differences in Table 1 are around 2 °C or very small.

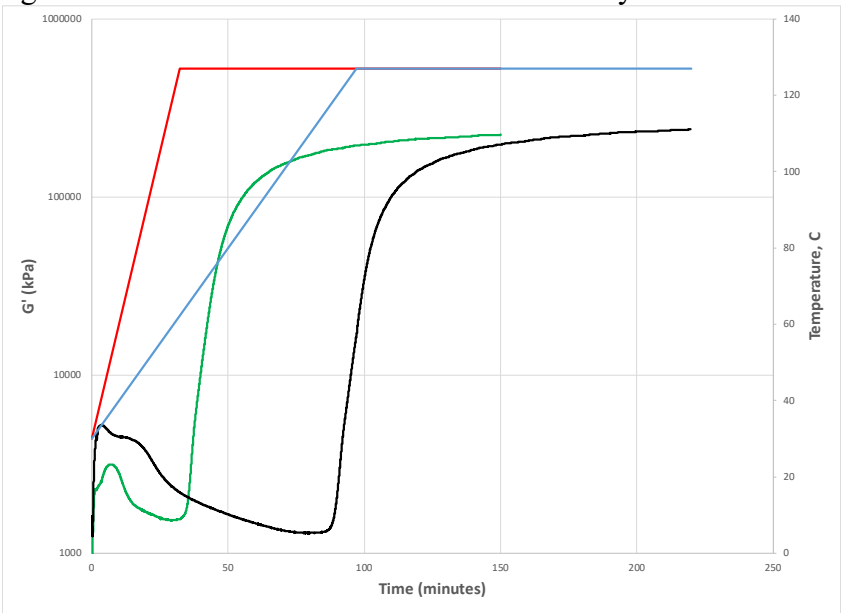

Figure 6. Cure of a prepreg at the same hold temperature but with two different ramp rates. Results show a similar cure curve shifted to longer cure times.

Figure 7 shows the cure of Prepreg No. 1 and No. 2 using the same ramp and hold temperature condition. The results clearly show that Prepreg No. 2 cures slower and produces a lower G' at

the end of cure at the processing temperature. Each prepreg can produce a distinct result to help characterize different prepregs and determine any effect from differences in the fiber, resin or aging.

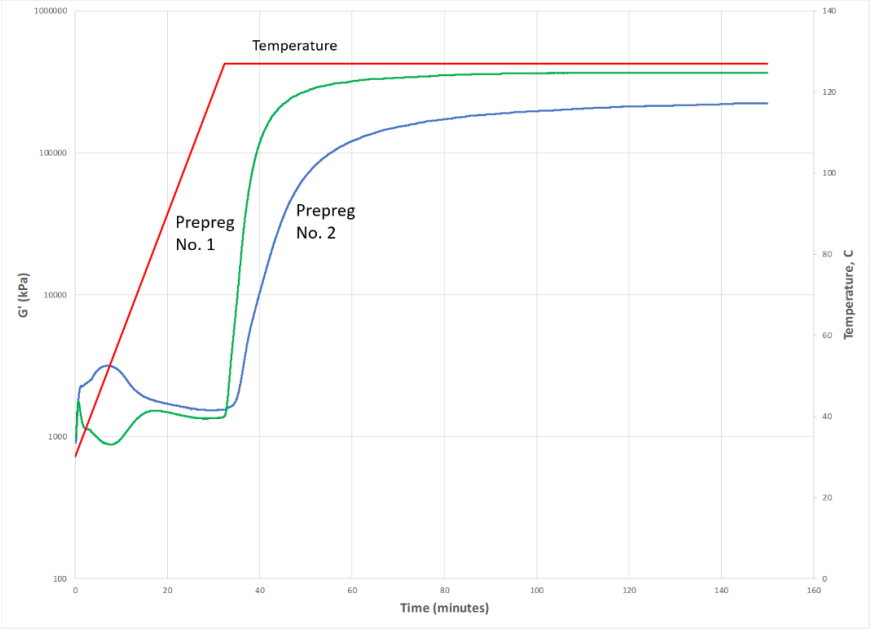

Figure 7. G' results during a ramp and hold for two different prepregs. Results show significant differences in the viscosity, cure rate and final modulus.

Isothermal Studies

Figure 8 shows Prepreg No. 2 tested under isothermal test conditions at four different test temperatures.

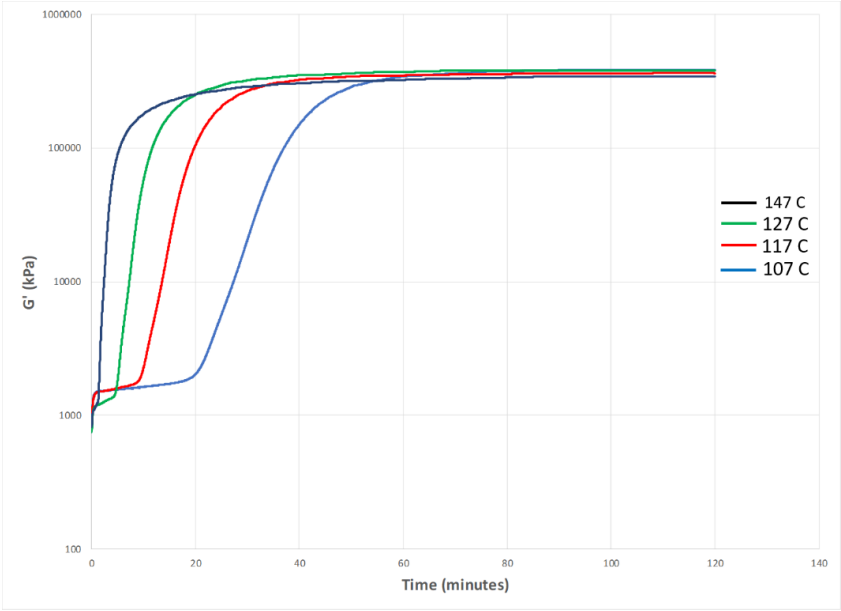

Figure 8. Cure of prepreg No. 2 at four different temperatures

As expected, the higher temperature produces the faster cure while the higher temperature also reduces the maximum G' value at the end of the cure at the hold temperature. Table 1 shows that the Tg changes significantly with increasing test temperatures. The Tg goes from 142 °C with cure at 107 °C to 184.1 C with cure at 147 °C. The result is a 42 °C increase in Tg with a 40 °C increase in the test temperature.

The advantage of isothermal processing is that the data can be applied to the Arrhenius Model of reactivity. The first step in analyzing the changes in mechanical properties shown in Figure 8 and calculating rate constants for the Arrehnius Model is to normalize the reaction curves [8]. The lowest G' during a test becomes 0.0 and the highest becomes 1.00 as shown in Figure 9.

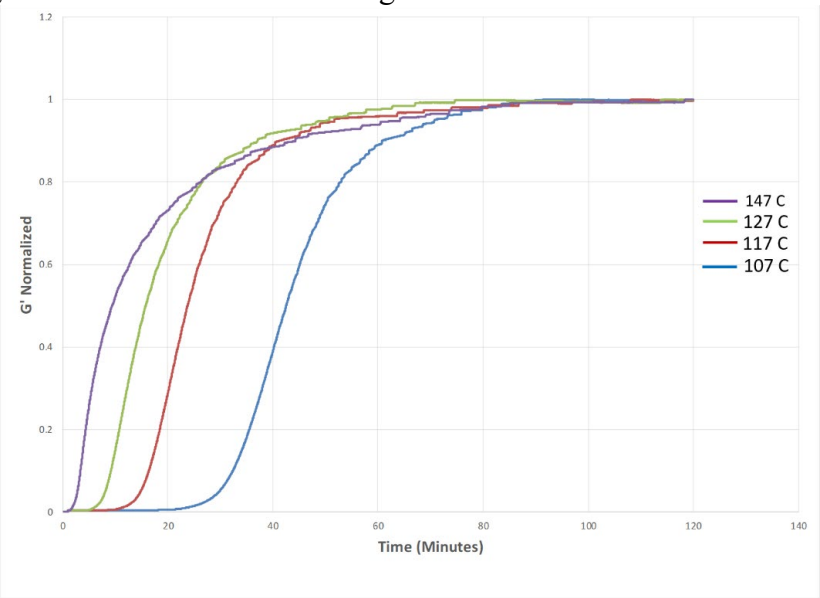

Figure 9. Normalized cure curves from Prepreg No. 2 determined from the results in Figure 8.

The fraction reacted is referred to as α so that the fraction not reacted becomes (1-α). For example, if 40% were reacted then α=0.40 and (1- α) becomes 0.60. This is needed because many reaction rates are directly affected by the unreacted material and not the final product.

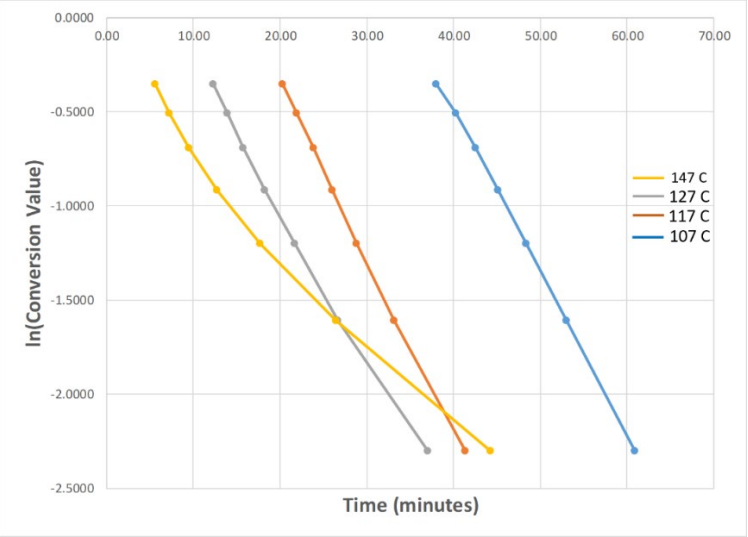

Figure 10. Ln(1-X) versus Time for Prepreg No.2

The value of ln(1- α) is plotted versus time with the expectation that it will be linear. The slope of the plot is the reaction rate constant k as shown in Figure 10. Table 2 contains the rate constants and the initiation times. Surprisingly, the rate constant k does not show a clear increase with every increase in temperature. The slopes are very similar. What changes more dramatically with temperature is the x intercept or t_i or initiation time. Figure 11 shows a plot of $\ln(t_i)$ versus the inverse Kelvin Temperature. The results for the three lowest test temperatures are very linear. The highest temperature had a distorted plot in Figure 10 and did not produce an initiation time that aligned with the other temperatures.

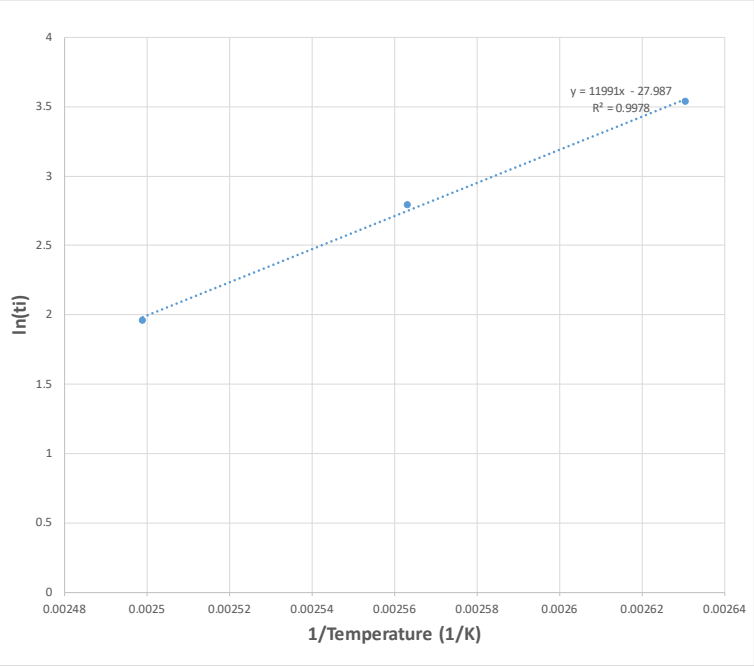

Figure 11. The initiation time for the reaction of prepreg No. 2 follows the Arrhenius Model even though the rate constants did not.

Figure 12 shows the isothermal cure curves from the Unidirectional Tape at three temperatures.

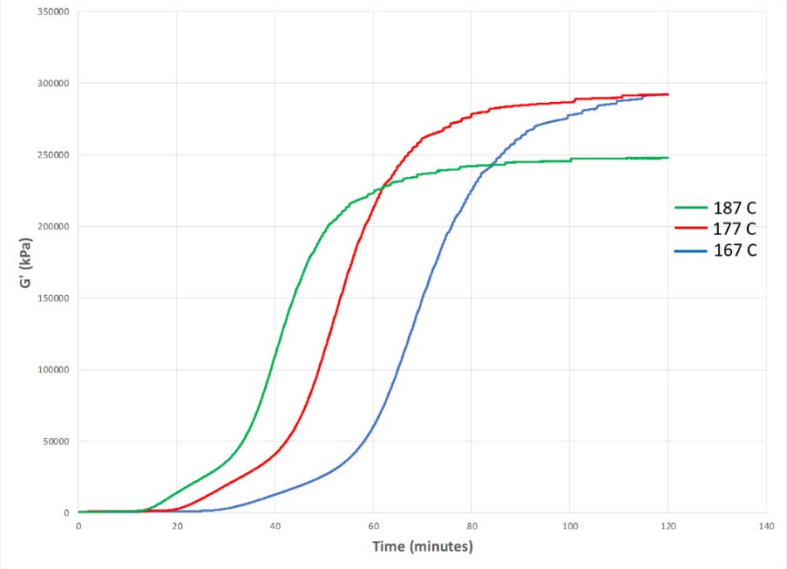

Figure 12. Isothermal cure curves from the Unidirectional Tape.

The Tg values in Table 1 show a significant increase with an increase in the isothermal test temperature.

The Tg value increased by 17 C for a 20 °C increase in the test temperature or slightly less than seen in Prepreg No. 2. Figure 13 shows the normalized cure curves and Figure 14 shows the plot of ln(1- α) versus Time for the Unidirectional Tape.

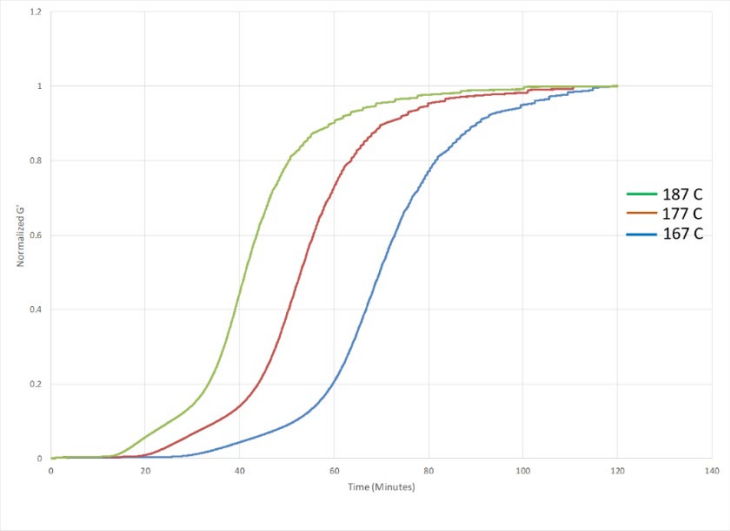

Figure 13. Normalized cure curves from the Unidirecitonal Tape results in Figure 12.

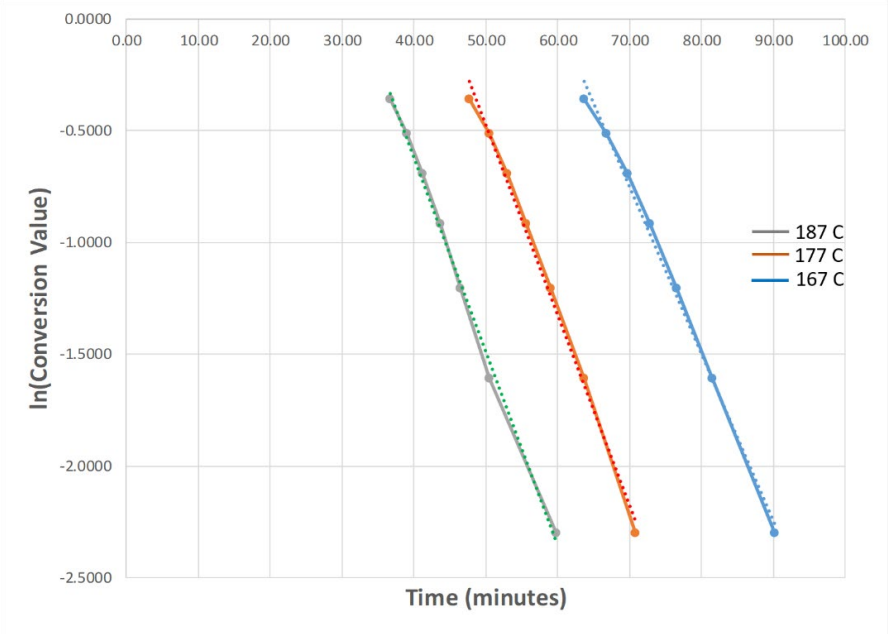

Figure 14. These plots were very linear, but the slopes did not change much with changes in temperature.

The rate constants taken from the very linear slopes did not show the expected change with increasing temperature. The rate constants are also in Table 2. Figure 15 shows the plot of the $\ln(t_i)$

versus the inverse Kelvin Temperature for the Unidirectional Tape sample. Again, the Initiation Time follows the Arrhenius Model.

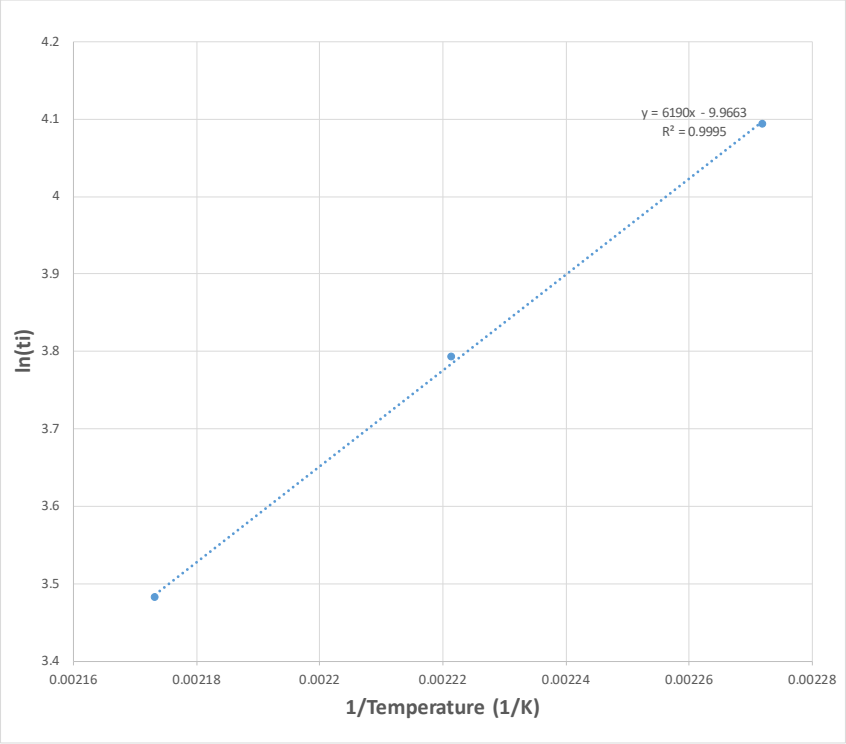

Figure 15. Again, the Initiation Time followed the Arrhenius Model very closely.

CONCLUSION

The ESR was used to analyze the cure of prepregs and a Unidirectional Tape. The results showed the viscoelastic properties of prepregs throughout the cure cycle while building a coupon that resembles a composite part. It can also characterize different prepregs based on the speed of the reaction and the mechanical properties at the processing temperature. An attempt was made to fit the reaction curves to a simple Arrhenius Model. The results showed a lot of evidence of a 1st order reaction but the model failed on a prepreg and a Unidirectional Tape sample because the rate constants did not increase as the temperature increased. However, the calculated Initiation Times did follow the Arrhenius Model. This result suggests that mechanical testing done by an ESR or similar instrument may be necessary to verify the actual kinetics of the prepreg cure, especially when dealing with multiple layers of a prepreg.

One prepreg showed very little change in Tg with change in the hold temperature. A second prepreg showed a significant change in Tg with a change in the isothermal cure temperature. The Unidirectional Tape sample Tg was also very sensitive to the isothermal test temperature and showed an increase with an increase in the processing temperature. The ESR appears to be capable of determining the presence of any unreacted materials in a prepreg cured under standard conditions using the final measured Tg. Further study can be conducted to evaluate the influence unreacted components may have on final product properties.

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Appendix

Table 1. Tg Values from All Samples and Temperature Profiles

	Prepreg Sample	Temperature Ramp C/minute	Hold Temperature C	Hold Time minute	Tg Max Tand C	Tg Max G" C
Non-Isothermal	1	3	127	150.0	137.3	134.5
	1	1	127	220.0	139.3	136.1
	1	3	117	150.0	138.8	136.8
	1	3	137	150.0	135.6	132.8
	2	3	127	150.0	177.3	164.4
Isothermal	2	0	107	120.0	144.4	142.0
	2	0	117	120.0	157.5	153.8
	2	0	127	120.0	179.9	164.9
	2	0	147	120.0	187.6	184.1
	Unitape	0	167	160.0	205.1	201.3
	Unitape	0	177	120.0	215.7	211.2
	Unitape	0	187	120.0	222.1	218.4

Table 2, Constants from 1st Order Arrhenius Model

Sample	Temperature C	Slope (k)	Intercept	Inititiation Time minutes	R
Prepreg No. 1	107	-0.0860	2.9501	34.30	0.9996
	117	-0.0929	1.5126	16.27	0.9992
	127	-0.0788	0.5583	7.08	0.9972
	147	-0.0494	-0.2140	------	0.9897
Prepreg No. 2	167	-0.0744	4.4559	59.92	0.9989
	177	-0.0845	3.7504	44.38	0.9989
	187	-0.0838	2.7238	32.51	0.9984