

## **Thermoset Curing Schedule and its Affect on the Final Properties**

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### **ABSTRACT**

Most thermoset resin manufacturers recommend a two step temperature cure schedule. The first temperature step generates the cross linking sites (or nodes) and prevents the sample from decomposing. The second temperature step binds the nodes together into a highly cross linked material. The material is not as susceptible to decomposition after the first step. This curing schedule gives a material with maximum cure and physical properties such as: modulus, thermal stability and delamination. A process engineer, striving to minimize the time in process, may decide to shorten, or eliminate, the first temperature step. Although this shortens the process time, it can have serious impact on the final properties of the material.

Measuring the final modulus of the cured specimen at room temperature is a good measure of the final cure state of the specimen. Since most of the commercial processes use large batches, it is not economically feasible to run large batches of test cure schedules. The average Dynamic Mechanical Analyzer (DMA) is ideally suited to measuring the modulus during the cure, but the sample's stiffness becomes too large for the DMA to measure the same cured specimen back at room temperature. The DMA/SDTA 861 is capable of measuring the shear modulus of a thermoset resin from the uncured state to the cured state, at high temperature, and the cured state back at room temperature. This paper will report the results of these tests as the cure schedule is changed.

### **INTRODUCTION**

Historically, Differential Scanning Calorimetry (DSC) has been used to measure the degree of cure. The heat of reaction needed to cure an uncured sample is taken as the measure of the heat required for a sample to be 100% cured. A sample that has been cured in a process is then run in the DSC and the residual heat of reaction (a small exothermic peak) is measured. Unfortunately, the DSC does not measure whether the heat is coming from linear or branching reactions. Of course, branching reactions are preferred for optimal mechanical properties.

The DMA can measure the modulus of the sample as it cures. If the sample reacts with more branching reactions, the modulus will be higher. The modulus, of course, is temperature, as well as degree of cure, dependent. The modulus that has the most meaning commercially is the modulus at room temperature after the cure. The Mettler-Toledo DMA/SDTA 861e has sufficient stiffness range to measure the lowest modulus (as the sample is heated prior to the first reaction) and the highest modulus (as the sample is returned to room temperature after the cure). Both the DSC 822e and the DMA/SDTA 861e were used in this study of epoxy curing.

There are many variables in a two temperature step curing schedule. We made some assumptions to simplify the experiments for this paper. First, the heating and cooling rates were fixed at 2 °C/min. This was selected to simulate the slow heating (and cooling) rate of commercial curing presses. Second, the total time of the experiment was fixed. In this way, the total time during the two isothermal temperatures was fixed at 90 minutes. Lastly, the low temperature step was fixed at 175 °C and the high temperature step was fixed at 250 °C. Four experiments were performed with the 175 °C step held isothermal for 10, 20, 30 and 40 minutes, and the 250 °C step was held at 80, 70 60 and 50 minutes, respectively. The questions to be answered in this study are as follows. Which curing schedule gives the most heat of reaction and the highest modulus at room temperature? Do DSC and DMA agree on the best cure schedule? If not, why?

## **EXPERIMENTAL**

### *Sample and Sample Preparation*

The sample used in these experiments was a fiberglass cloth filled epoxy prepreg. The sample was a proprietary material and its exact composition is unknown. The sample was in sheet form with a release layer on each side. The specimen for both DMA and DSC was cut into a disk with a hole punch and the release layers removed. The thermal analysis method, as shown in figure 1, was designed to have a constant total time, but vary the amount of time spent at the low and high temperatures for curing. The thermal cycle for both the DSC and the DMA were as follows:

- Ramp at 2°C/min from 30 °C to 175°C
- Hold Isothermal at 175 °C for X minutes
- Ramp at 2 °C/min from 175 °C to 250 °C
- Hold isothermal at 250 °C for 90-X minutes
- Ramp at 2 °C/min from 250 °C to 30 °C
- Hold isothermal for 10 minutes (DMA only)

Note: The value of X was 10 for method #1, 20 for method #2, 30 for method #3 and 40 for method #4.

### *DMA Procedure*

The sample disk was placed and centered on the shear clamps. The sample thickness was measured by difference after it was loaded on the shear clamp plates. The diameter was measured after the first experiment was complete and the shear clamps were opened. The first data file was modified to reflect this new sample diameter. The subsequent samples were tightened in the shear clamps to the same thickness and the diameter was assumed to be the same as the first scan. The DMA experiments were run at 10 um oscillation amplitude, a frequency of one hertz and a maximum dynamic force of 35 N. When the sample becomes so hard that the 35 N of force has been reached, the DMA reduces the amplitude so the force is held constant at 35 Newtons. The specimens retained they appearance after all of the experiments. This is an indication that the samples did not decompose during the experiment.

### *DSC Procedure*

The disk was placed in a 40 uL aluminum crucible and hermetically sealed for the DSC experiments. The specimen was run twice. The first scan was used to cure the sample. The second scan was used to subtract the baseline heat capacity from the first scan.

## **RESULTS and DISCUSSION**

### **DSC Results**

The time-temperature profile for each of the experimental methods is shown in Figure 1. The methods are all similar except for the time spent in each of the isothermal regions. A typical DSC result is shown in Figure 2. The heat flow reaches a maximum at about the same time the method reaches the isotherm at 175 °C. The reaction slows, but continues all through the experiment. Baseline subtraction is made difficult by the complex method with isotherms and temperature ramps. The best baseline is simply to run the same specimen through the same method a second time. Figure 3 shows both the first and second scans plotted together. The space in between these curves represents the heat of reaction. Figure 4 shows the result after baseline subtraction. Again, the heat of reaction is plainly seen as an exothermic shift in the heat flow curve (black line) above the zero value (black dashed line). We used the running integral of the DSC heat flow curve for easiest comparison to the DMA results, Figure 5. Figure 6 shows an overlay of all the DSC experiments plotted versus heat flow. Figure 7 shows the running integral for all the DSC experiments. Method #2 (black line), with 20 minutes isothermal at 175 °C, had the highest total heat of reaction, at about 1300 J/g. Method #2 gives the largest enthalpy of reaction and hence the most cure, as measured by DSC.

### **DMA Results**

Now let's switch over to the DMA tests. Figure 8 shows why the DMA/SDTA 861 is so valuable in this test. The modulus (black line) goes through seven orders of magnitude during this experiment. The vertical dashed line marks where the DMA automatically switches from strain controlled to stress controlled. This occurs at about 90 minutes and without any interruption or artifact in the modulus (black line). The sample becomes its softest at about 60 minutes into the run when the modulus reaches its minimum. At this point the DMA is using only 90 micro Newtons of force to maintain 10 um of oscillation amplitude. The motor reaches the user selectable (35 N in this experiment) at about 90 minutes. From this point onward the DMA holds a constant 35 N of force amplitude and allows the displacement amplitude to decrease as the sample stiffens further. The displacement amplitude drops as low as 1 um at the end of this experiment.

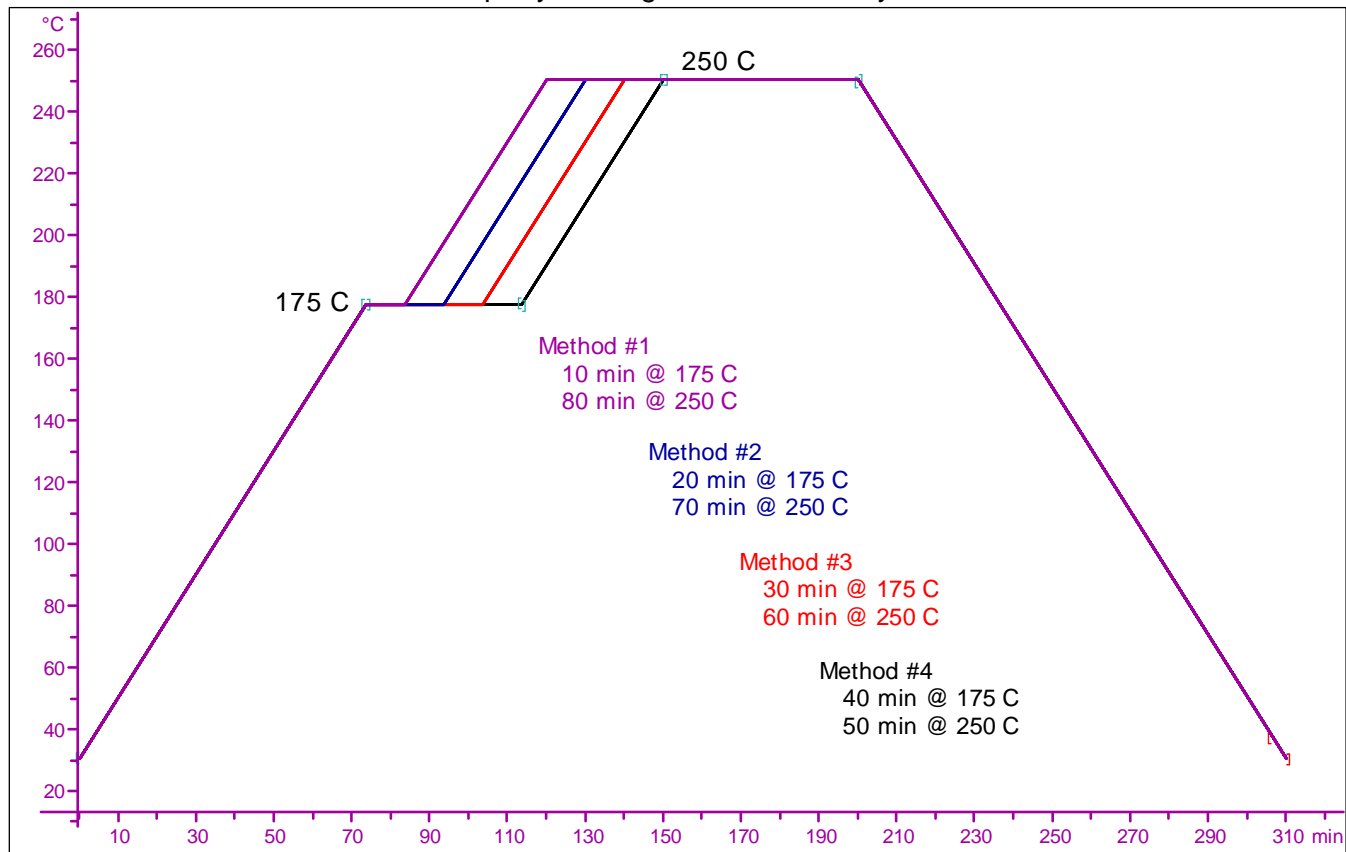
The DMA experiment is very repeatable as seen in the replicates shown in Figure 9. These curves were two runs on different specimens of the same sample. As you can see, the modulus value is very repeatable through the entire experiment. The step increase in the modulus, at about 280 minutes, is due to the glass transition ( $T_g$ ) of the cured specimen as the temperature is decreasing back to room temperature. Figure 10 shows the  $T_g$  for all four methods. As you can see, neither the  $T_g$  magnitude nor the temperature changes very much for the four curing methods. The  $T_g$  by DMA is often used as a test for the degree of cure of a thermoset. These results indicate the opposite.

### **Comparing DSC and DMA Results**

All the results are plotted in Figure 11. The DMA results indicate that method #4 (40 minutes isothermal at 175 °C) gave the best cross linking with a final modulus of almost 1.1 GPa (blue dashed line). The DSC results indicate that method #2 gave the highest degree of cure at almost 1300 J/g (black solid line). This comparison can also be seen more clearly in Figure 12.

## **SUMMARY**

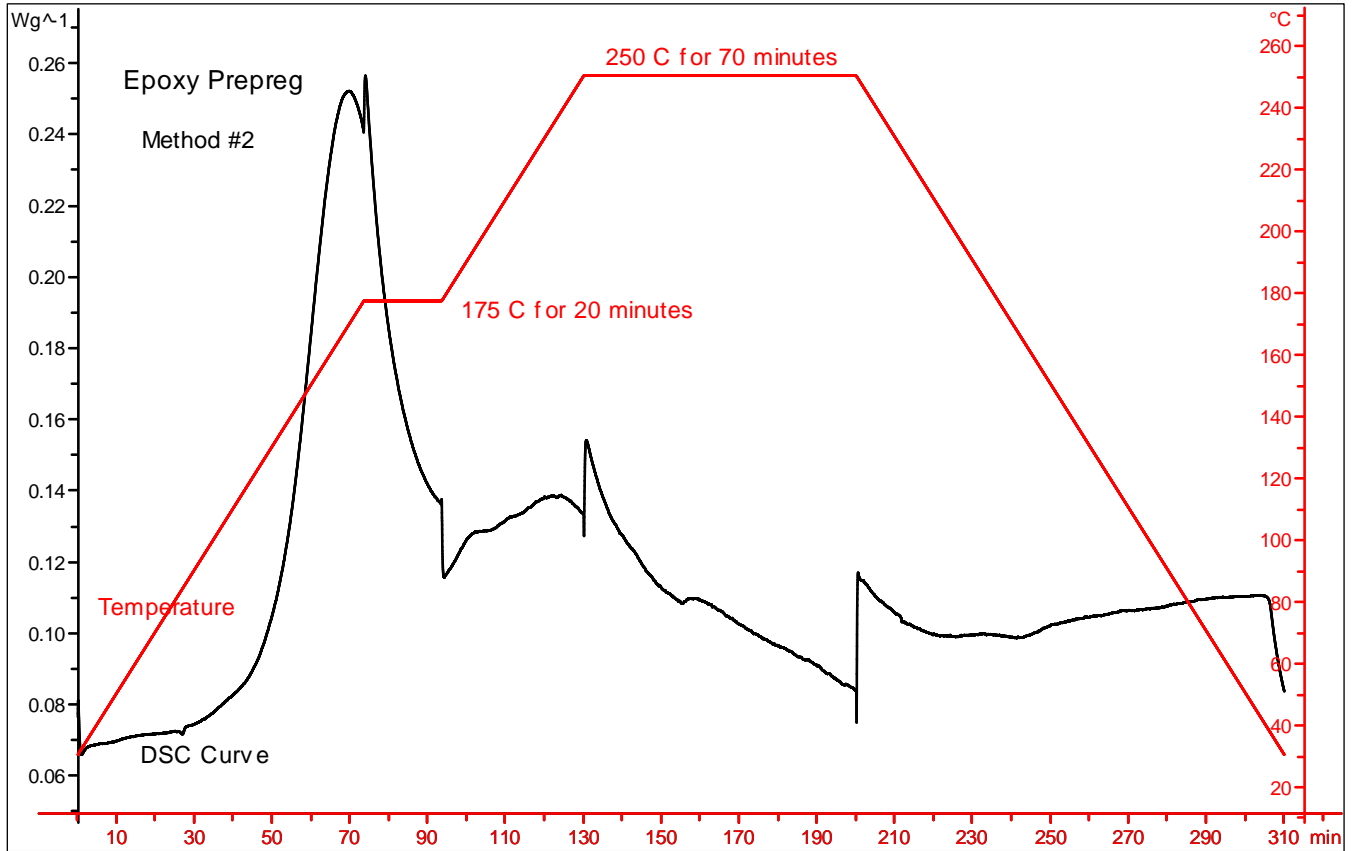
While the DSC does measure the total heat of reaction, it cannot distinguish between linear reactions and cross linking reactions. So a sample that has a large heat of reaction may not have a large amount of cross link sites. Cross linking sites are needed to obtain the highest modulus. The DMA/SDTA 861 is the preferred method for optimizing curing conditions in order to reach the maximum stiffness for any given formulation.



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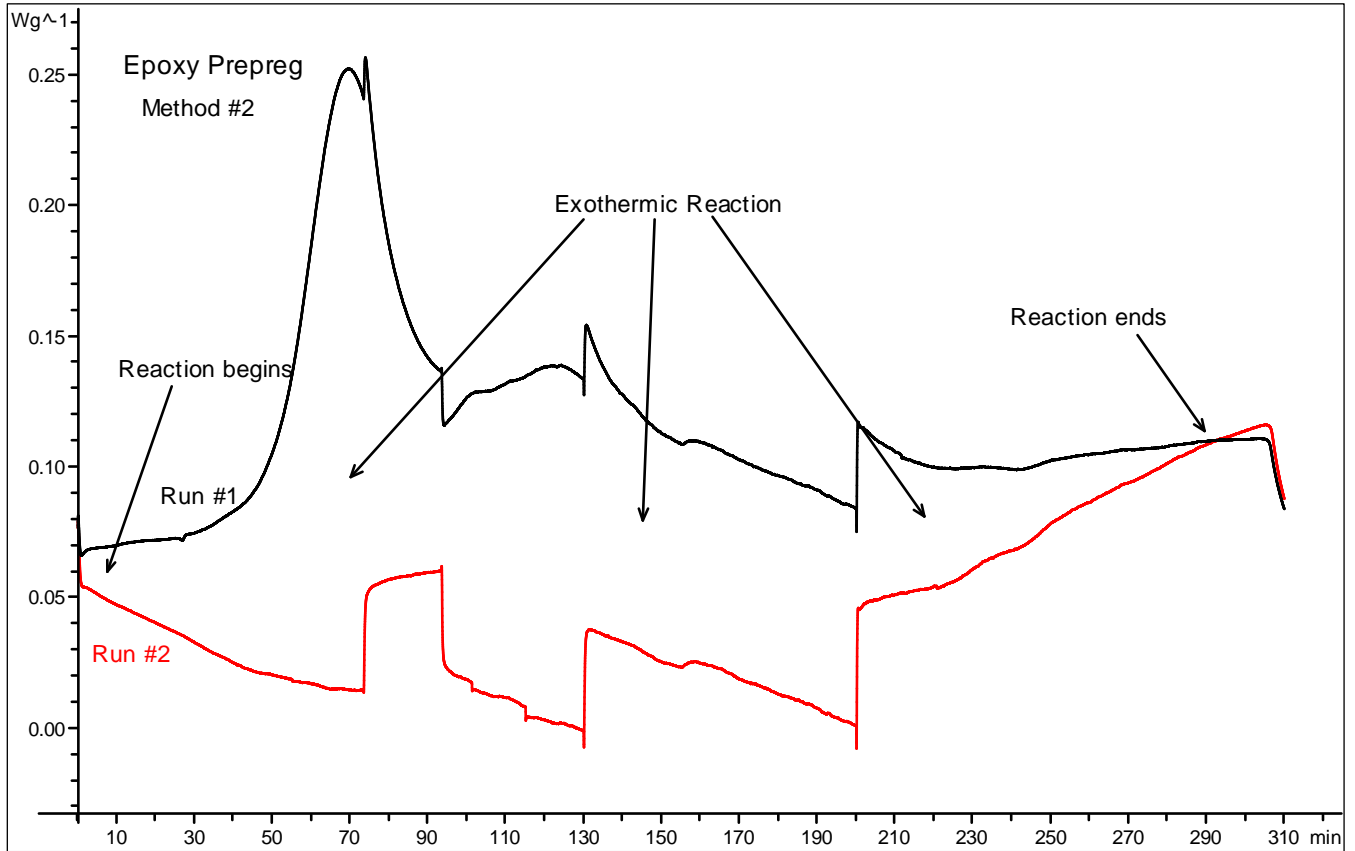
Figure 1: Temperature profiles for the four curing methods used in this paper for both DSC and DMA experiments.



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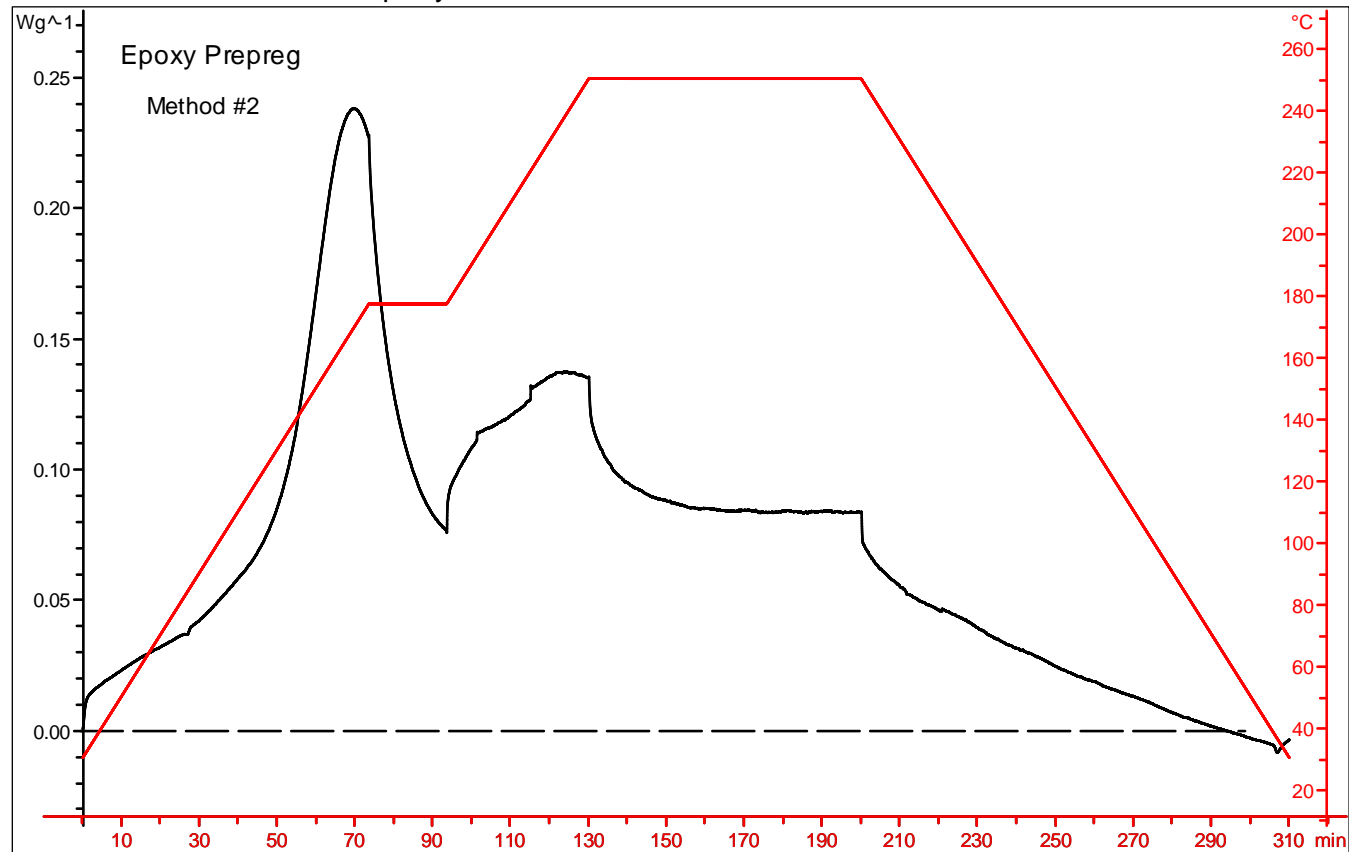
Figure 2: This is a typical DSC scan of the epoxy curing. The heat of reaction is confounded with the heat capacity of the sample during the temperature ramped portions of the method.



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Figure 3: This figure shows both the first (black) and second (red) scans. The difference between scans is the exothermic heat of reaction. Notice the sample is still curing as the sample temperature is decreased back to room temperature, region above 210 minutes.

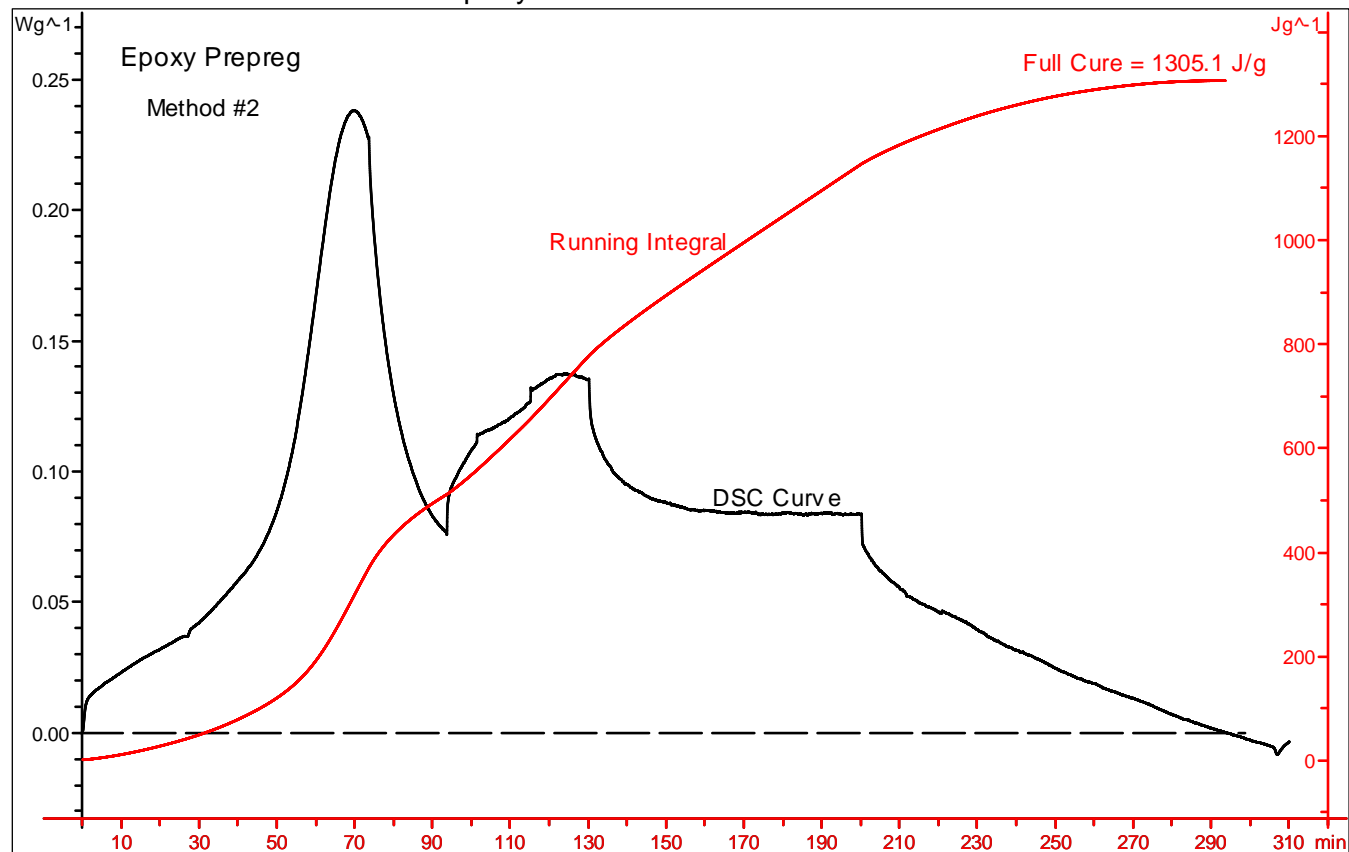


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Figure 4: This is a typical curing profile after subtraction of the second scan. The black curve is heat flow and the red curve is the sample temperature.

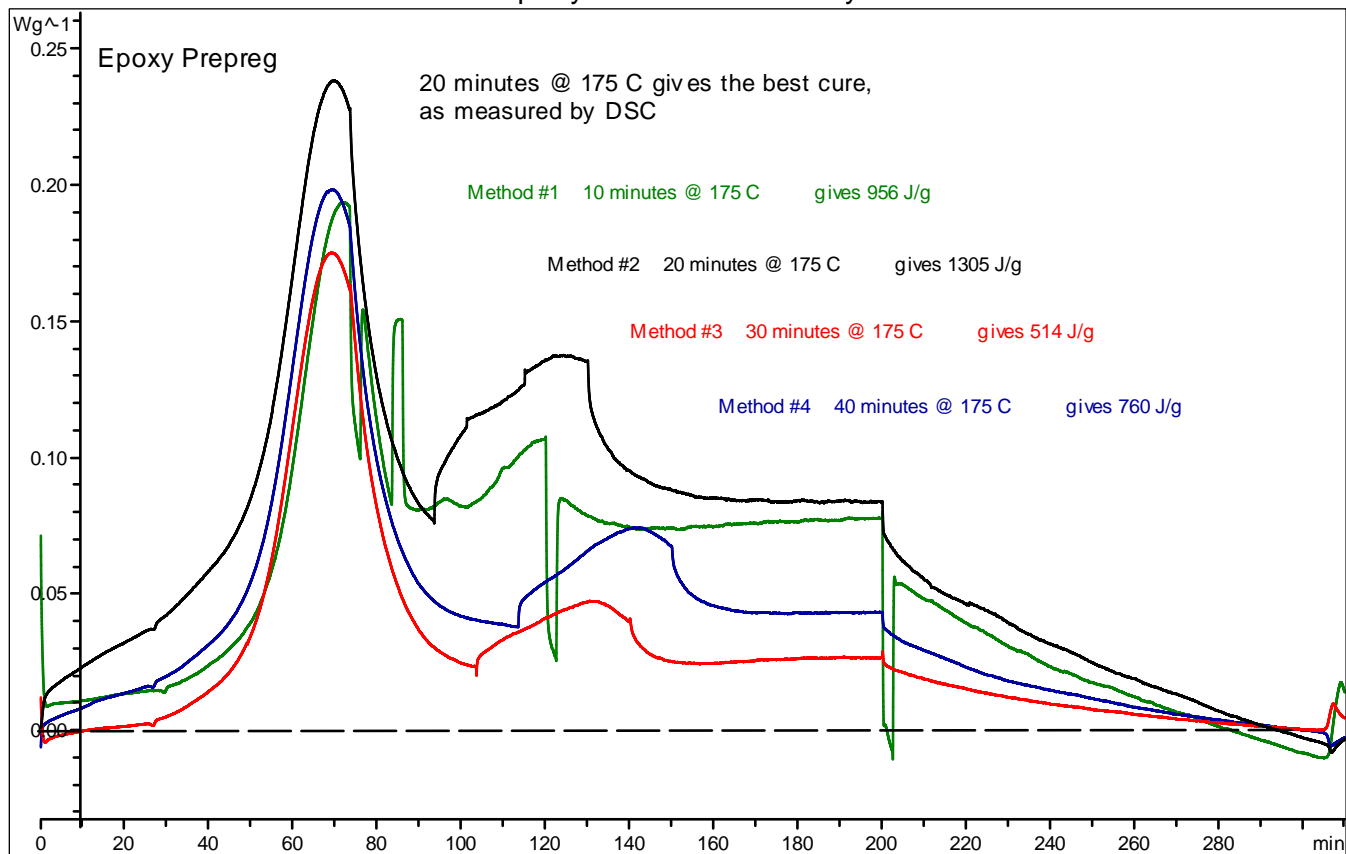




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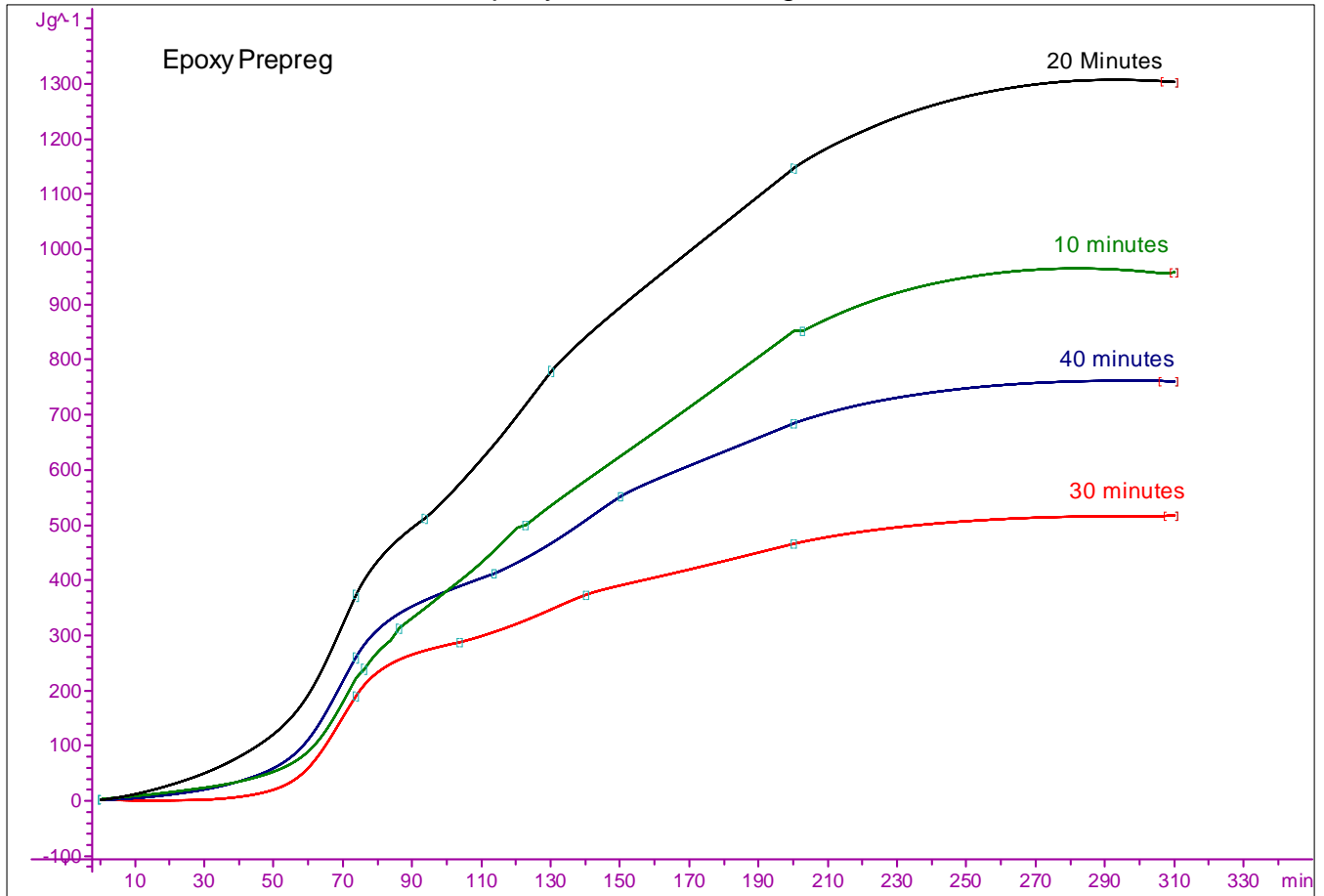
Figure 5: This is the running integral (red curve) for the area of the heat flow (black curve) above zero heat flow. The baseline is at zero heat flow because the baseline (second scan) has already been subtracted from the data.



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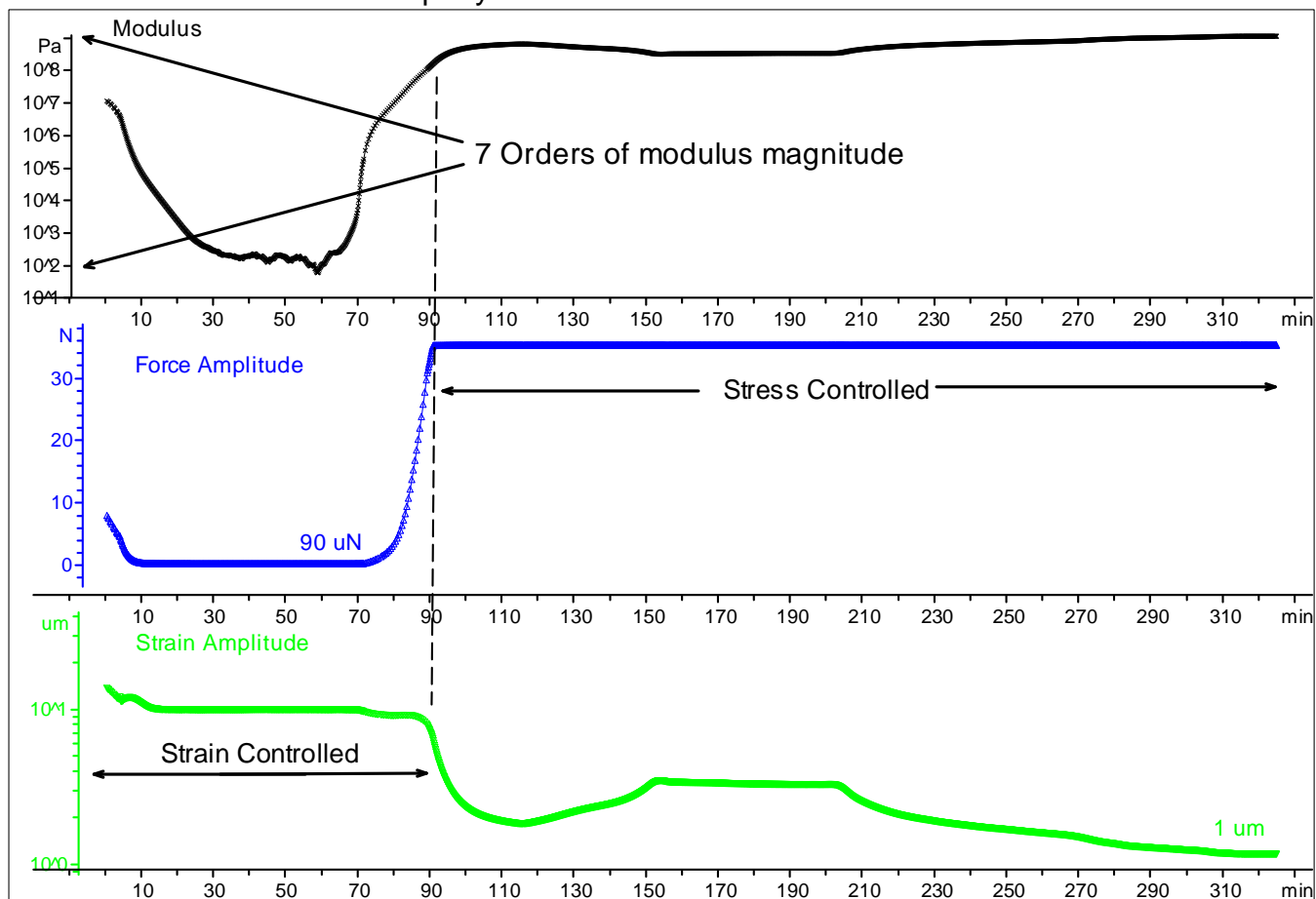
Figure 6: These are the DSC curves (baseline subtracted) for each of the methods.



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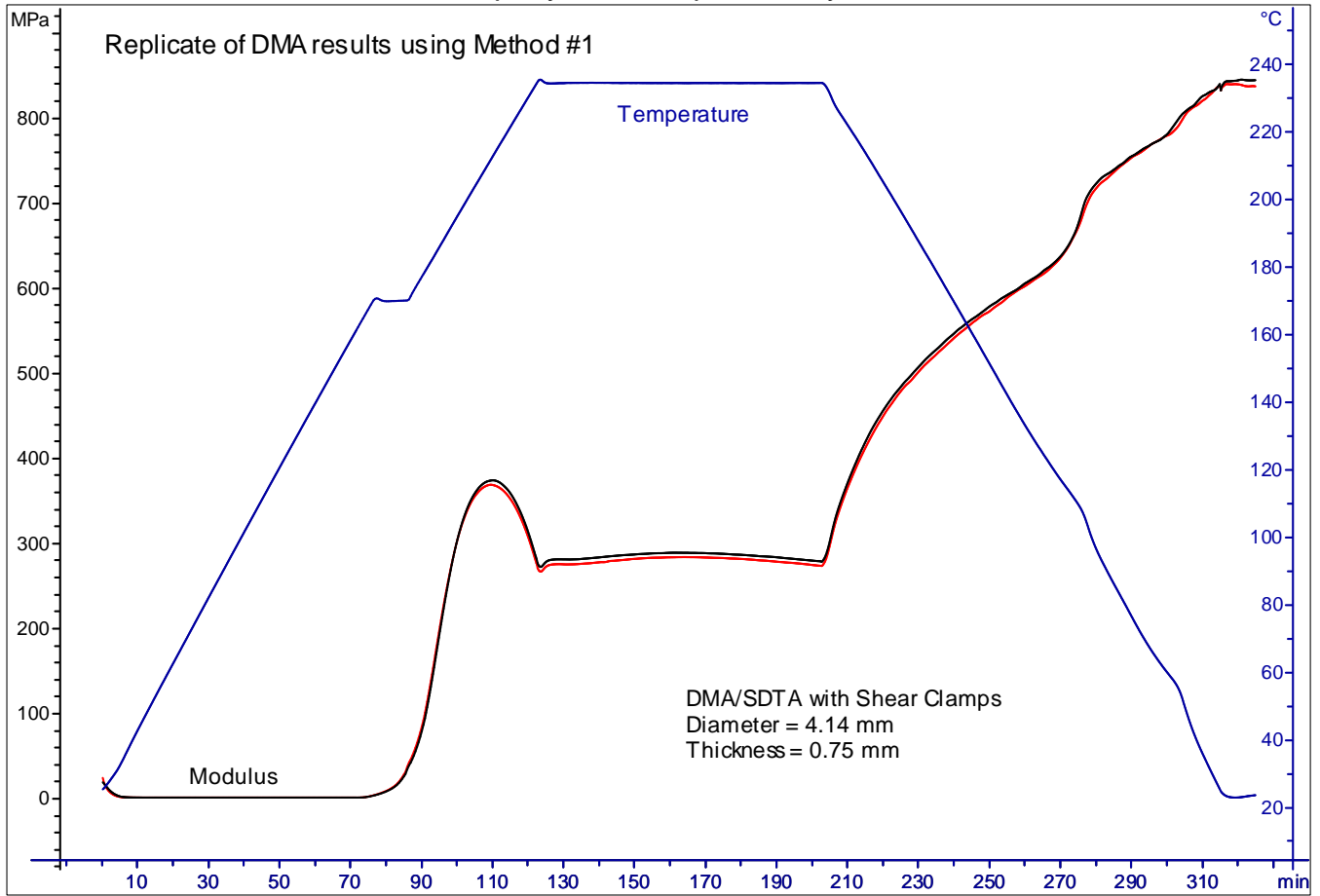
Figure 7: These are the running integrals for the four methods. Method #2 with 20 minutes isothermal at 175 °C has the highest cure, as measured by DSC. Method #1 is the green curve. Method #2 is the black curve. Method #3 is the red curve. Method #4 is the blue curve.



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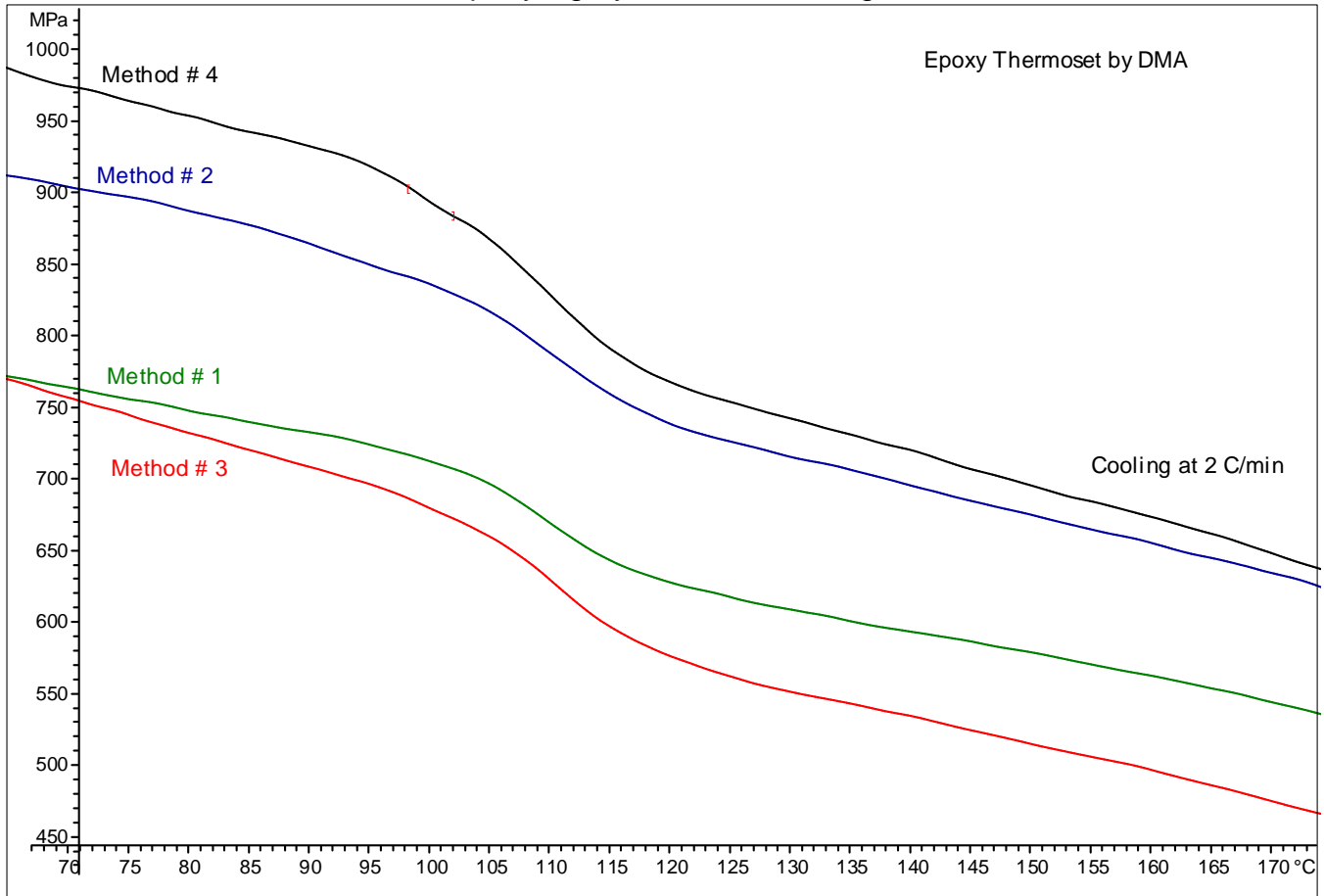
Figure 8: Typical stress (blue curve) and strain (green curve) profile for one of the experiments. The change between strain and stress control occurs at 90 minutes with no visible change in the calculated modulus (black curve). The stress is measured as low as 90  $\mu$ N (at 70 minutes) and the strain is measured as low as 1  $\mu$ m (at 325 minutes).



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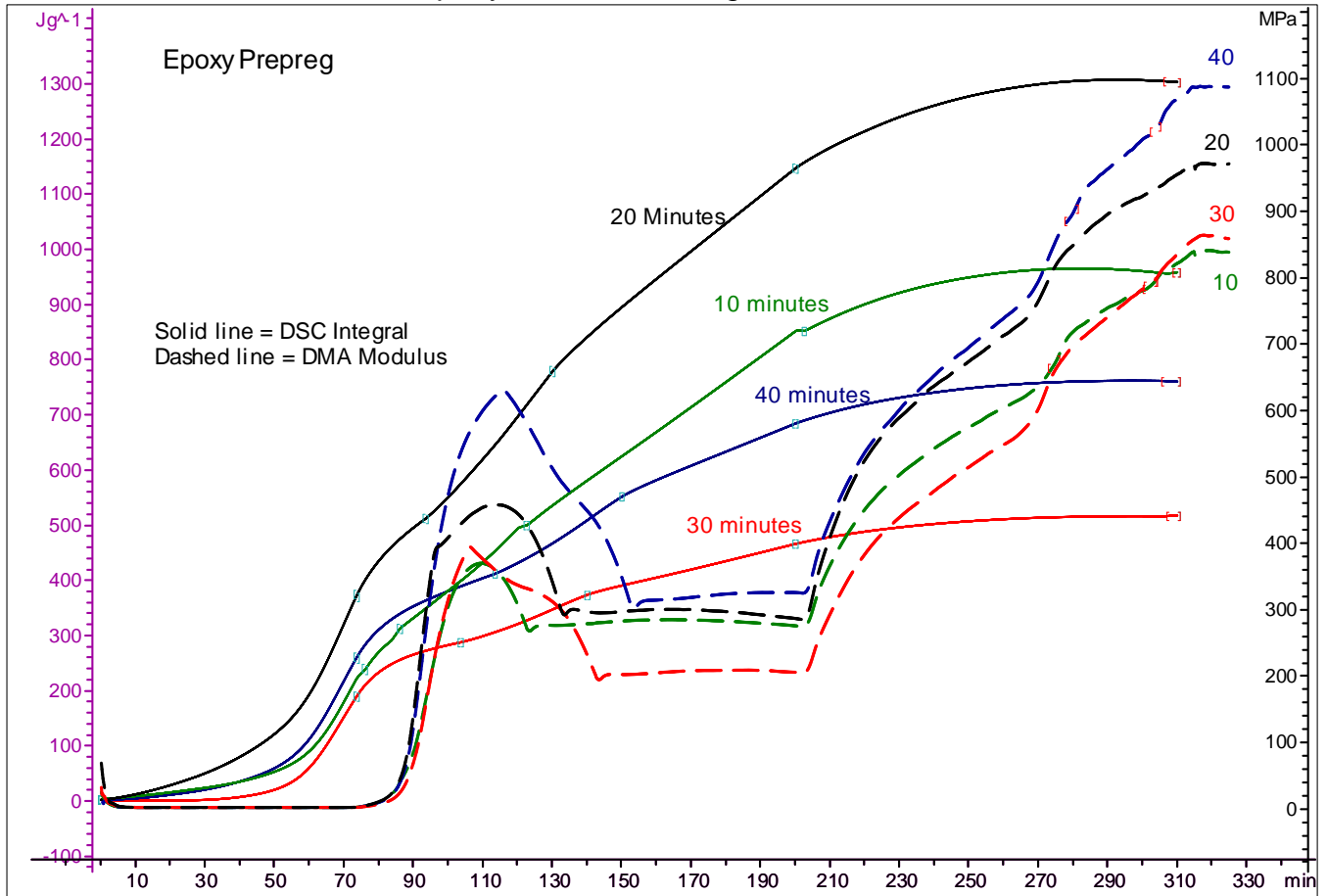
Figure 9: This is the data from a repeat of method #1 (red and black curves). The blue curve is the sample temperature as measured by a thermocouple in direct (metal to sample) contact with the sample.



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Figure 10: These curves are the modulus values as the sample ramps back down through the glass transition after the reaction. These curves were collected on cooling the sample at 2 °C/min.



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Figure 11: This is a comparison of the DMA (dashed lines) and the running integral from the DSC (solid lines). The DSC results indicate that the method #2 gives the high degree of cure since it has the highest reaction enthalpy of 1300 J/g (solid black line at 310 minutes). The DMA results indicate that method #4 gives the highest degree of cure since it has the highest modulus at almost 1100 M Pa (Dashed blue line at 310 minutes).