CHARACTERIZING THERMOSET CURING USING RHEOLOGY

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ABSTRACT

Studying the mechanical property changes accompanying a curing reaction is one of the most challenging rheological tests on account of the significant changes in sample properties during the curing process. In a typical thermoset cure, the change in modulus and viscosity can be as large as 6-8 orders of magnitude and can take place over short durations. This poses unique challenges for the experimentalist as the measurement torque can go from the instrument minimum in the pre-cure state to the maximum post-cure. As a result, one set of fixed test parameters cannot be used for monitoring the entire curing process. In this paper, we provided guidance for designing appropriate rheological test methods for curing analysis and elaborate on the importance of critical test parameters such as strain and axial force for achieving accurate and reproducible results. We concluded by comparing different approaches to quantify the gel point measurements and present results from gelation kinetics analysis.

1. INTRODUCTION

Thermosetting materials like epoxies are widely used in a number of diverse applications. These range from surface coatings in the aerospace and electronics industries to advanced composites, structural adhesives, and packaging materials. Compared to thermoplastic polymers, thermoset processing involves an irreversible chemical crosslinking reaction, making it ideal for use in the production of permanent parts that can withstand high temperatures without deforming. In addition, thermoset materials possess high mechanical strength, dimensional stability and good solvent resistance [1-3], offer design flexibility, and can be processed using reaction injection molding to produce parts with varying wall thickness.

The performance of the thermoset products is greatly influenced by processing parameters such as chemical composition, cure temperature and cure time. Several thermal and mechanical techniques have been successfully employed to study and characterize the curing process. These include Differential Scanning Calorimetry (DSC), rheology, Dynamic Mechanical Analysis

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(DMA), Dielectric Analysis (DEA), Thermo-Mechanical Analysis (TMA) and Thermo-Gravimetric Analysis (TGA) [4-8]. Among them, DSC is one of the most popular techniques, especially in the study of cure kinetics [9-13], since thermoset curing is an exothermic process that is marked by clearly defined events in the thermogram. DSC analysis of epoxies can reveal information about the degree of cure/ cure conversion, heat capacity change, and the glass transition of the cured product. However, the rate of the cure process, also called gelation, cannot be detected by DSC [13]. This piece of information, critical for optimizing process conditions, can be quantified through rheological analysis, which provides a direct measurement of the material's mechanical properties through viscosity (η, η*), viscoelasticity (G*, G' and G") and damping factor (tan δ).

A schematic representation of the changes occurring during a curing reaction are presented in Figures 1 and 2. At the start of the cure process (a and b), the reaction gradually builds up the sample's molecular weight, progressing from small molecule monomers to oligomers which go on to form polymers and branched polymers. During this process, sample's viscosity increases exponentially as the reaction proceeds. At the gel point (c), a sample spanning network is formed coinciding with the first appearance of infinite molecular weight. At this point, the system loses solubility and the zero-shear viscosity (η) diverges towards infinity (Figure 2). Beyond the gel point, reaction continues to drive towards a complete network formation (d). This is reflected in the ongoing changes in physical properties such as modulus (G) that continue to increase and attain levels characteristic of a fully developed solid network (Figure 2).

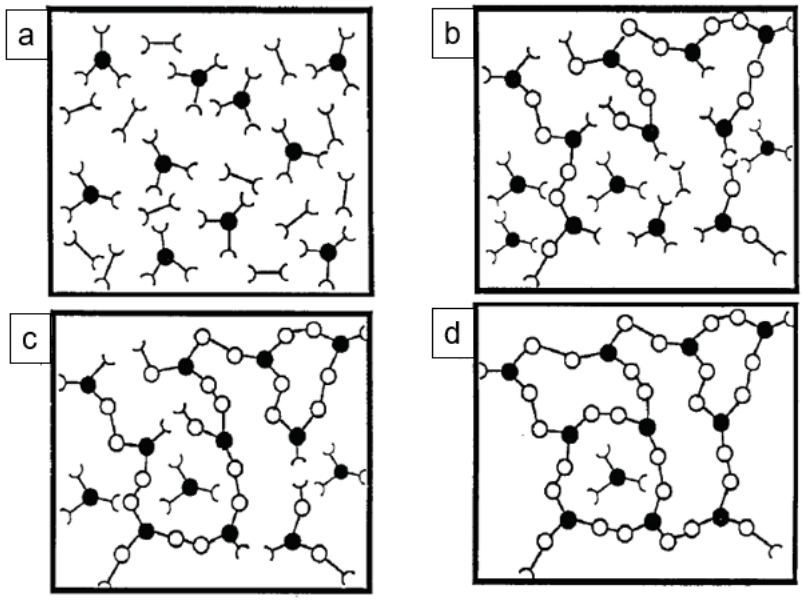

Figure 1 Representative schematic of different stages in chemical curing: (a) Multifunctional monomers; (b) Linear growth and branching below gel point; (c) Gelled but incompletely crosslinked network; (d) Cured thermoset solid.

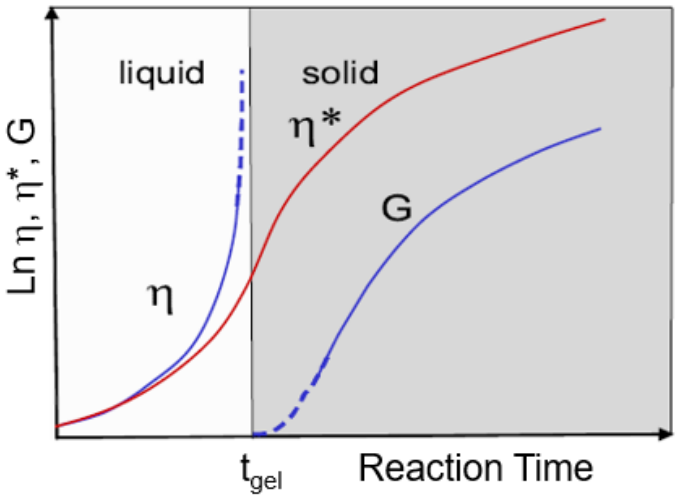

Figure 2 Typical evolution of rheological profile during thermoset curing depicting two distinct regimes demarcated by t_{gel}.

The rheological profile of the thermoset curing reaction can be divided into two stages demarcated by the gel point. Before gelation, the sample's shear viscosity (η) is the most informative parameter; after gelation, storage modulus (G') is the key parameter for monitoring the changes of mechanical property in the glassy state. Therefore, the gel point is one of the most important kinetic characteristics of curing and rheological analysis traces the entire network formation process [14-15] from start to finish.

During a curing process, the changes in physical property such as viscosity and modulus can be large as 6-8 orders of magnitude over the course of the test. This broad change in material properties poses some unique challenges for experimental design, since the material can rapidly transition from a low viscosity fluid into a high modulus solid. In general, the rheology of liquid samples with low viscosity is tested using a large diameter geometry (e.g., 40 mm) and a suitably large oscillation strain in order to obtain a good signal to noise ratio. On the other hand, high modulus-high stiffness solid samples are tested using a small diameter geometry (e.g., 8 mm) at small strains to stay within the cured material's linear viscoelastic region and avoid overloading the instrument torque. As a result, a set of fixed test parameters are not suitable for monitoring the entire curing process. This has constrained the range of reported rheological test data in a number of previously published studies, where only one part of the process – either the beginning of the curing [14-16] or the end of the curing [2,3,5] – were investigated.

In this paper, we present rheological results that continuously monitor the entire curing process, from start to finish. Specifically, the importance of choosing and optimizing certain critical test parameters are discussed in detail. Next, we highlight the effectiveness and benefits of using a dynamic multi-wave test method for measuring the true gel point in thermosetting materials and conclude with a discussion on determining the gel activation energy from rheological data.

2. EXPERIMENTATION

2.1 Material

A commercially available two-parts epoxy was used in this test. The epoxy resin was bisphenol A; a mixture of aminoethyl piperazine curing agent and non-reactive nonyl phenol accelerator formed the curing component. This combination is commonly found in commercially available two-part epoxies [17]. Samples were prepared with 50/50 mix at ambient temperature before loading to a rheometer for analysis. At this mix ratio, this specific epoxy sample is rated to cure over 30 minutes at ambient conditions, making it ideal for demonstrating experimental designs in this study.

2.2 Rheological measurements

Curing experiments were performed under both isothermal and non-isothermal conditions using a Discovery Series HR-3 rheometer (TA Instruments, New Castle, DE). In this study, all rheological measurements were performed under small amplitude oscillatory shear conditions, where the rheometer applies a sinusoidal deformation on the sample. At small deformations, the resulting material response is also sinusoidal and can be either in-phase or out-of-phase with the applied deformation. Such oscillatory experiments reveal important information about the material properties through parameters like storage modulus (G'), loss modulus (G"), complex viscosity (η^*) and loss tangent ($\tan \delta$) Here, the storage modulus represents the elastic component of the material; the loss modulus captures the viscous component. Together, these two parameters characterize the viscoelastic behavior of the material.

The rheometer was equipped with the Environmental Test Chamber for temperature control and 25mm disposable parallel plates were used for all tests. First, isothermal curing tests were performed at temperatures of 50°C, 60°C, 80°C and 100°C; a fresh sample was used for each test. Next, temperature ramps were performed from -10°C to 100°C at a heating rate of 2°C/min. All experiments were programmed with an initial strain of 0.05 % applied at 1 Hz frequency. The strain was setup to automatically adjust to the material changes through either the Auto-Strain or Non-Iterative sampling features available on the Discovery HR-3 rheometer. Any axial forces generated due to sample shrinkage during the curing reaction were compensated by actively controlling the axial force control to within 0 +/- 0.1N during the experiments.

An additional set of multi-wave experiments were performed on an ARES-G2 rheometer (TA Instruments, New Castle, DE). In a multi-wave experiment, the instrument simultaneously applies a combination of different test frequencies during a single oscillatory cycle. The rheometer automatically resolves the resulting rheological parameters into the individual test frequencies, providing a quick and simple approach for collecting data at multiple frequencies in the same time as a single frequency test. The multi-wave was programmed at an isothermal temperature of 80°C at the fundamental test frequency of 10 rad/s and a strain of 10 %. The higher harmonics were programmed at strains of 2% and 1% at frequencies of 50 rad/s and 100 rad/s respectively. The peak strain in the combined multi-wave was 12.5%, which is within the linear viscoelastic region of the epoxy sample. In these experiments, the rheological parameters were monitored as a function of time and temperature.

3. RESULTS

For epoxy and other thermoset materials, the formation of a crosslinking network structure can be monitored using a dynamic rheological measurement. This can be done as an isothermal time sweep or a dynamic temperature ramp. Figure 3 shows a representative result of the rheological profile of an epoxy material cured at an isothermal temperature of 80°C. The data show that the physical properties of this epoxy sample undergoes significant change during curing. At the beginning of the test, the sample's loss modulus (G") is greater than the storage modulus (G') indicating that the sample is an easily flowable low viscosity liquid – this is also reflected in the magnitude of the complex viscosity(η*). As the sample cures, all key rheological parameters – G', G", and η* – show a rapid increase over time. At around 204 seconds, the G' and G" curves crossover delineating the point at which the sample undergoes a liquid-to-solid transition, which is also described as gelation. Beyond this crossover point, the sample loses flowability and is dominated by a solid like response. At longer times when the curing reaction goes to completion, the complex viscosity, G' and G" curves reach a plateau and the sample behaves like a rigid solid.

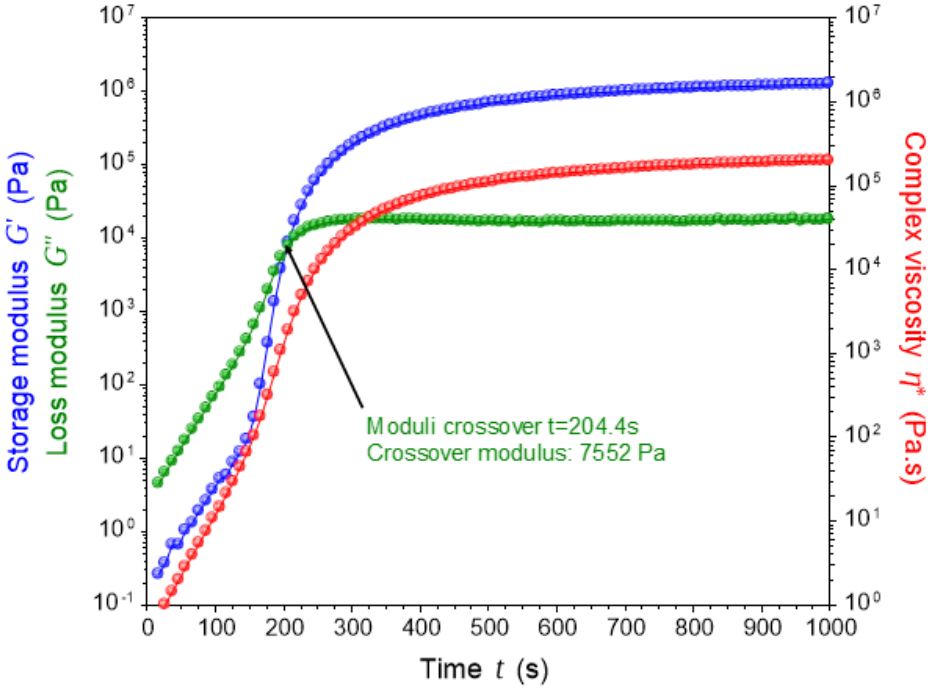

Figure 3. Isothermal epoxy curing at 80 °C.

For this epoxy sample, it is notable that the storage modulus G' of the sample increased by nearly 7 orders of magnitude through the curing reaction. Obtaining good rheological data is challenging in tests where there is a dramatic change in the material properties. The following sections provide additional details about these issues and specify solutions to overcome them and obtain good reproducible results.

3.1 Automatic Strain Adjustment during Thermoset Curing

The epoxy sample studied in this paper shows drastic changes in rheological properties on curing, a profile that is very typical for thermoset cure (Figure 3). At the beginning of the test when sample shows low viscosity, a large oscillation strain ensures good measurement signals. However, once the sample is cured into a high stiffness and modulus material, a small strain is recommended in order to maintain the measurement torque within the instrument specifications. Additionally, small strains are required to avoid cracking the sample after it is cured. The key to obtain a good measurement result throughout this entire curing is to be able to adjust the measurement strain. The Discovery HR-3 rheometer with TRIOS software provides two options to the operators for dynamic strain adjustment. The first method is called "Non-iterative sampling" and is available in all oscillatory test procedures. The second method is called "Auto-Strain" and is available for use on rheometers equipped with Continuous Oscillation or Direct Strain Oscillation – this feature allows exceptional levels of strain-controlled oscillations without the use of complicated feedback loops, even on instruments that natively operate through stress control.

3.1.1 Non-Iterative Sampling for Strain Adjustment

The Non-iterative sampling option is designed specifically for use in tests like thermoset curing where rapid measurements on an evolving sample take priority over precise strain control. In this mode, the rheometer software continuously monitors the torque and stress values during the test and predicts the torque required to obtain the target strain based on the previous data point. Figure 4 demonstrates how Non-iterative sampling works to adjust the strain during an isothermal curing test. The test procedure was programmed with a small oscillation strain of 0.05% for the measurement. This strain was determined to be within sample's linear viscoelastic region throughout the test by performing a strain sweep on a fully cured sample (data not shown). However, since the sample viscosity before curing is very low, using a small strain of 0.05% at the start of the test would lead to noisy data.

Under Non-iterative sampling, the operator is asked to specify a "lower torque limit" to ensure that the rheometer always operates at torques higher than the entered value (e.g. 5 μNm). If the oscillation torque required to control at 0.05% strain is lower than 5 μNm at any point during the test, the instrument directly operates in torque control at 5 μNm for that point. This invariably results in oscillation strains greater than 0.05% but ensures that the instrument is operating at a reasonable torque value that gives good rheological data. This behavior is seen in the initial part of the test when the sample viscosity is low. As sample cures, the increase in viscosity and modulus leads to a steady reduction in the oscillation strain resulting from a torque of 5 μNm. At around 200 s, the strain resulting from 5 μNm torque reaches 0.05%. From this point onwards, the instrument directly controls the strain amplitude at the programmed value of 0.05% for the rest of the measurement. In this manner, the rheometer collects good data over the entire duration of the test, by automatically switching between torque- and strain- control when appropriate, without any requiring any intervention by the operator.

When setting up this "lower torque limit" value, it is important to verify that the maximum strain imposed on the sample remains inside the linear viscoelastic region, especially when operating in torque-controlled mode. The imposition of large strains outside the linear region can

have an adverse impact on gelation times and the final modulus if a high value is programmed for the lower torque value. As a general guideline, a range of 2-5 µN.m is a good starting point for this field. This value can then be increased or decreased based on the data quality and the maximum oscillation strain encountered in the test.

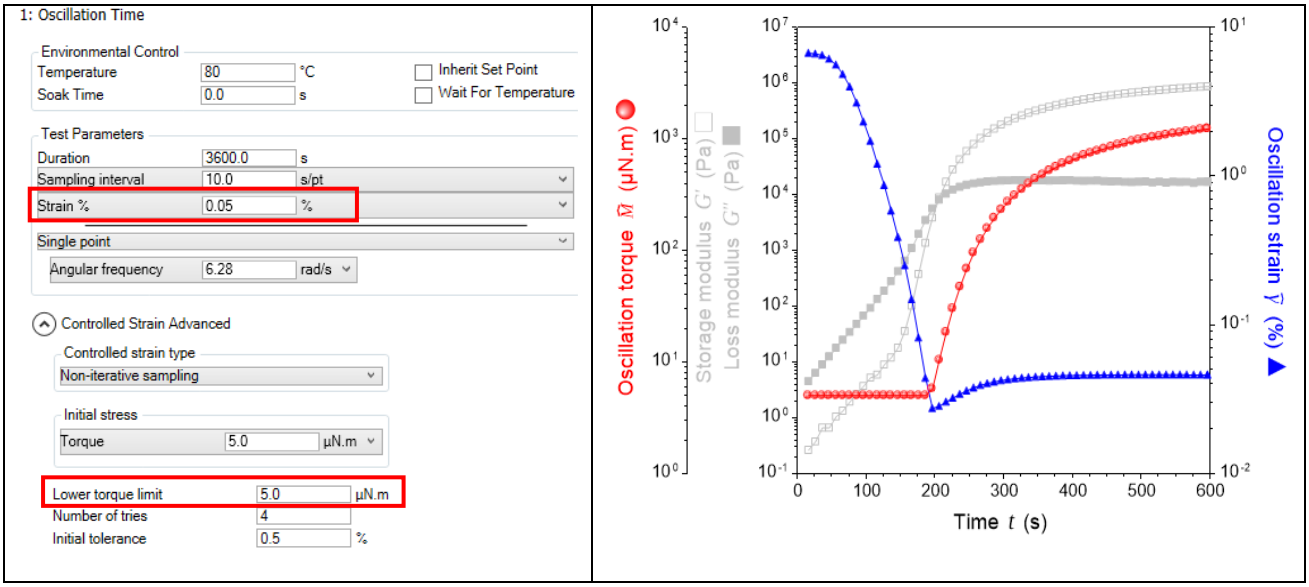

Figure 4. Demonstration of Non-Iterative Sampling feature for adjusting oscillation strain during a curing experiment: test settings and data from isothermal epoxy cure at 80 °C (see Figure 3).

3.1.2 Auto-Strain Feature for Strain Adjustment

Modern rheometers also offer Auto-Strain capabilities where the instrument automatically adjusts the oscillation strain during the test. Compared with Non-iterative sampling, Auto-Strain operates exclusively in strain control – the oscillation strain is dynamically adjusted to stay within a user-specified torque or stress window. We illustrate the concept of Auto-Strain on the same epoxy material cured using a temperature ramp. This type of curing profile is typical for prepreg materials where the thermoset epoxy or polymer is embedded in a reinforcing fabric or composite fiber matrix. Prepregs have optimal epoxy content that ensures the best cured properties and excellent uniformity within the cured part.

The curing of prepreg materials is initiated by temperature and can be studied using a controlled temperature ramp on the rheometer. During a temperature ramp, the physical properties of the sample first changes from a paste-like soft solid to a low viscosity liquid, and then onto a fully cured, high-stiffness solid. In this case, the "Auto-strain" feature automatically adjusts the strain, increasing or decreasing it as needed to adapt to the changes in sample properties. Figure 5 shows an example of an epoxy temperature ramp curing profile. The sample was loaded at -10°C and was heated up to 100°C at a controlled heating rate of 2 °C/min; the sample was then held at 100°C for an additional 10 minutes to complete the curing reaction. The results show that the sample starts off as a flowable viscous paste at -10 °C – at this point, the sample's loss modulus is greater than the storage modulus. As the temperature increases, the sample's complex

viscosity decreases by nearly three orders of magnitude before reaching an inflection point at around 1347 seconds and 35 °C. The epoxy's curing reaction is now initiated, leading to a rapid increase in the rheological properties at higher temperatures. At around 2406 seconds and 70.4 °C, the storage and loss moduli signals crossover, marking the gelation point and material's transition from liquid to a cured solid. Vitrification sets in after this point, causing a sustained increase in the storage modulus before it eventually plateaus by the end of the test.

Three critical process parameters can be obtained from this type of experiment: the minimum viscosity, the G'/G" crossover gelation time, and final cured modulus. The minimum viscosity relates to the epoxy's flowability and is a critical parameter for quality control. Batches with very minimum low viscosity can bleed out of the edges, but those with high minimum viscosity will not flow evenly and can have adverse impacts on the quality of the finished product. The minimum viscosity is directly related to the epoxy's processing window and can be directly tuned through altering the formulation.

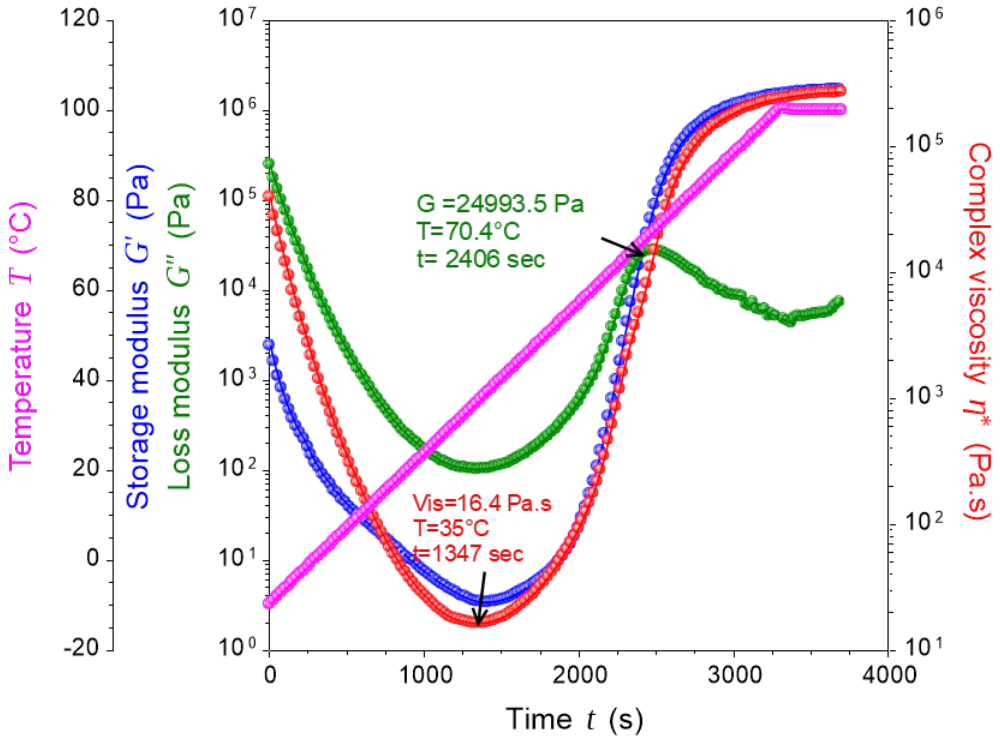

Figure 5. Temperature ramp curing of epoxy sample at a heating rate of 2°C/min.

In this temperature ramp measurement, the initial test strain was set at 0.05%, with Auto-strain torque limits of 5 µNm and 500 µNm (shown in Figure 6). This torque window is not the window of the instrument specification, but a user-specified range of torque values specific to this experiment. Auto-strain provides a smart way to automatically adjust test strain during the temperature ramp test. At the beginning of the temperature ramp, the oscillation strain is maintained at 0.05%. With increasing temperature, the complex viscosity and moduli decrease

rapidly, and the oscillation torque required for controlling 0.05% strain drops below 5 µNm, which triggers the Auto-strain feature. Starting from the next data point, the oscillation strain is increased by 30% based on the values programmed in the "Strain adjust" setting. This ensures that the measurement torque would not go below this operator selected minimum torque limit. Once the sample starts to cure at temperatures above 35 °C, the viscosity and moduli increase sharply within a narrow temperature window. This increase in rheological parameters is accompanied by a concurrent increase in the oscillation torque as well. When the torque required to control the current strain exceeds 500 µN.m, the programmed upper torque limit, the Auto-strain feature starts to decrease the oscillation strain by 30% in subsequent data points. The strain continues to decrease as long as the measurement torque is greater than the user-specified upper torque limit. The selection of this torque window is integral to effectively utilize the rheometer's Auto-strain feature as the limits determine whether the sample strain is within the linear viscoelastic region throughout the entire measurement, even when the material viscosity drops.

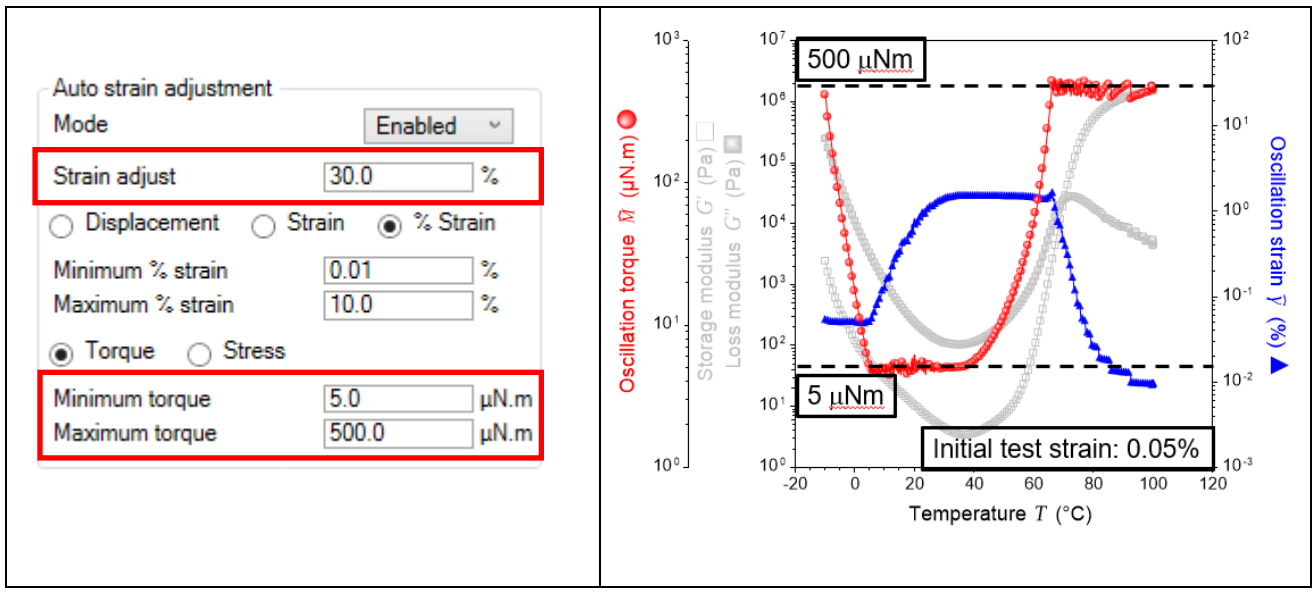

Figure 6. Demonstration of Auto-Strain feature for adjusting oscillation strain during a curing experiment: test settings and data from temperature ramp-initiated cure (see Figure 5).

The two approaches for dynamic strain adjustment outlined in this section offer valuable tools for the rheological testing of thermosetting materials. Non-iterative sampling automatically switches between strain and torque control and only requires two user defined parameters to program the test – the oscillation strain and the minimum torque limit. For thermosetting materials, the programmed strain must be the oscillation strain that has to be applied at the end of the test, once the sample has fully cured. This value can be determined through a strain sweep test on a fully cured sample. Auto-strain offers a more advanced approach to strain adjustment and operates exclusively by changing the strain to stay within user-specified strain and torque limits. The multiple parameters available in this mode give the user a great deal of flexibility to adjust and tune the strain adjustment response to specific systems. For both cases, the representative parameters used in this study are suitable for the rheological study of most

thermosetting materials and offers good initial values for other groups looking to study these materials.

3.2 Measuring Sample Shrinkage through Axial Force Adjustments

When a thermoset material cures, it undergoes some volumetric shrinkage especially during vitrification stage. This type of behavior is typically observed in cases where the curing reaction takes place quickly – here, the rate of the crosslinking reaction is faster than the relaxation time of the polymer chains. This generates residual internal stresses in the cured product that can lead to defects such as sample warpage and dimensional inaccuracies. As a result, it is critical to quantify the extent of sample shrinkage for repeatable control over manufacturing processes and predictable product performance [18].

The rheological measurement can be used to monitor and quantify the extent of sample shrinkage during the cure process. This is accomplished by activating the axial force control in a test procedure – details are presented in Figure 7. In general, it is good practice to always enable axial force control during curing reactions to avoid accidental overloads of the rheometer's force transducer. During the curing measurement described in Figure 3, the instrument was programmed to maintain an axial force of 0 N on the sample, with a +/- 0.1 N sensitivity window. As the sample cures and it starts to shrink, it exerts a force on the upper plate of the rheometer. If this force is larger than the axial force control parameters, the rheometer head adjusts the gap to release the shrinking force and maintain 0 N force on the sample. Therefore, the change in gap during the test directly quantifies the amount of sample shrinkage and can be correlated to the degree of cure through independent DSC measurements [19, 20]. Such cure-induced sample shrinkage is directly influenced by the rate of the reaction and can be controlled by adjusting the temperature or initiator to tune the speed of the process.

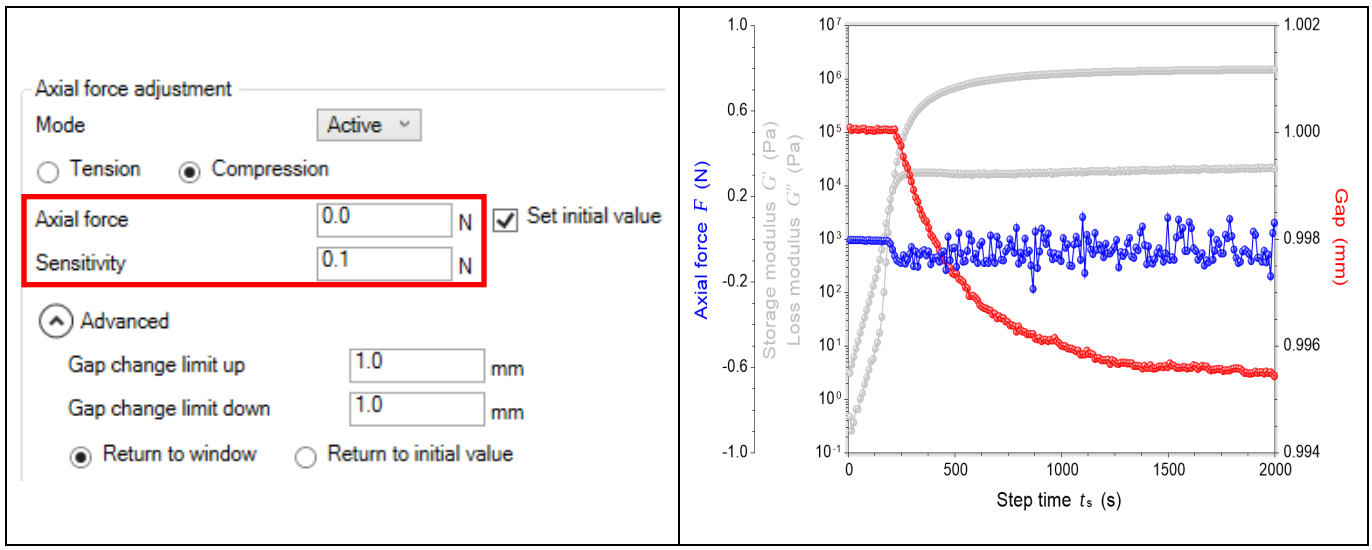

Figure 7. Use of Axial force adjustment to monitor sample shrinkage: test settings and data from isothermal epoxy cure at 80 °C (see Figure 3).

3.3 Gel Point Measurement and Gelation Kinetics

3.3.1 Multi-wave Analysis for True Gel Point Measurement

The "gel point" is one of the most important characteristics of thermoset curing and, as previously discussed, separates the polymerization and crosslinking process of network formation. One commonly accepted definition of the "gel point" is the time or temperature where G' and G" curves intercept and tan (δ) =1 (example shown in Figure 3). In general, most rheology tests, including curing, are conducted using a single frequency such as 1 Hz. While this approach is suitable for practical purposes such as product qualification, it represents a somewhat simplistic view of the curing process and may not be applicable for all samples. For example, the initial sample structure in some prepreg samples results in G' > G" throughout the test. In such cases, a crossover point is not present, complicating the use of this metric for gel point identification.

Winter *et al.* [21] have pointed out that using the G'/G" crossover point to describe gel point is only satisfied if stress relaxation in the critical gel follows a power law of $G(t) = t^{-1/2}$. In their paper, Winter *et al.* detail a more precise method to define the true gel point by identifying the intersection of the tan(δ) curves measured at different frequencies. Determining the true gel point of a thermoset in this manner typically requires multiple experiments at different oscillation frequencies. However, running multiple experiments requires preparing multiple samples and has the potential to introduce variation due to differences in sample loading and trimming techniques. In addition, this approach can also be time-consuming, especially for slow curing systems.

The rheological multi-wave test method provides an opportunity for obtaining the same information in a single experiment by simultaneously applying multiple frequencies. The multi-wave test method continuously tracks the material at multiple frequencies at each data point, making it ideal for studying the temporal evolution of thermosetting materials. In a multi-wave experiment, the rheometer applies the oscillation deformation at a fundamental frequency and at user-specified higher harmonics of this fundamental. For example, for a fundamental frequency of 10 rad/s, the 5^{th}, and 10^{th} harmonics would correspond to frequencies of 50 and 100 rad/s, respectively. The applied strain is simply a summation of the individual oscillations at the specified amplitudes and is schematically represented in Figure 8.

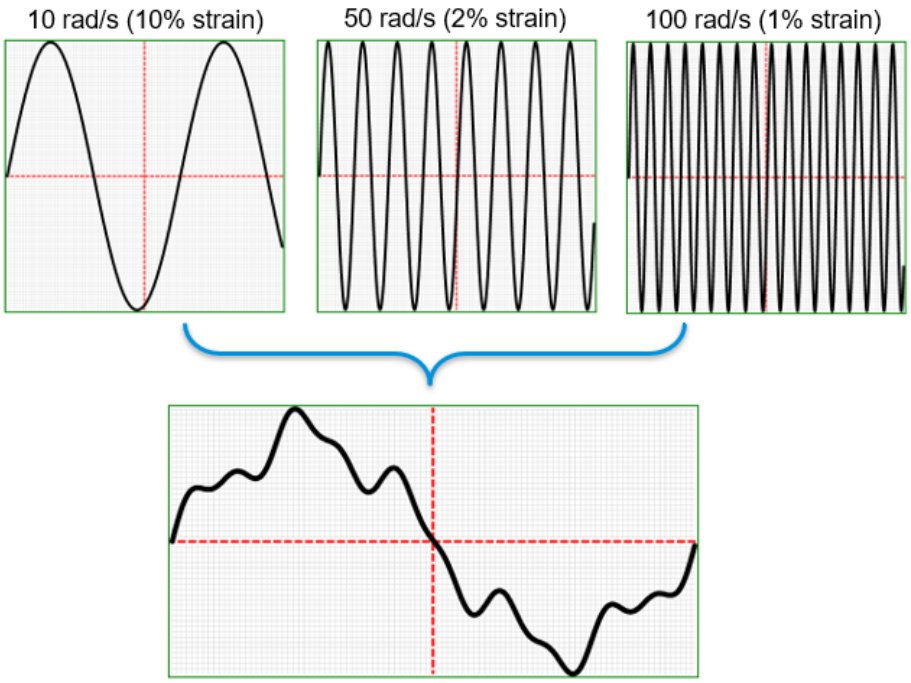

Figure 8 Multi-wave oscillation strain profile, formed by additive summation of 10 rad/s fundamental frequency at 10% strain with 5th and 10th harmonics (50 rad/s at 2% strain, 100 rad/s at 1% strain).

Following the method elucidated by Winter *et al*., a multi-wave test was programmed at a fundamental frequency of 10 rad/s; higher harmonics were selected at 5 and 10 times the fundamental frequency. Advanced rheometers like the ARES-G2 give the user complete control over the multi-wave profile – the strain applied at each harmonic can be individually tuned to ensure that the total strain is within the linear region of the sample. Further, it is also possible to apply a phase offset to the higher harmonics as well – this helps in maintaining the total strain of the combined multi-wave within the linear region and in easier deconvolution of the data by separating the peak amplitude at different harmonics.

The raw data from the multi-wave experiment is presented in Figure 9 as a function of time – the three vertical points at each time point represents the simultaneous collection of data at the three frequencies in the multi-wave (10 rad/s, 50 rad/s and 100 rad/s). The material response to the applied multi-wave strain is automatically deconvoluted into the individual frequencies and the measured data points are simultaneously correlated to extract the elastic and viscous moduli for all the excitation frequencies applied in the multi-wave. The raw data were subsequently split into 3 separate time sweeps at frequency of 10, 50, and 100 rad/s using the TRIOS software. This is presented in Figure 10a, where the data are equivalent to overlaying three separate isothermal cure experiments at each frequency. Figure 10b demonstrates the effectiveness of multi-wave testing to identify a true gel point where the tan(δ) data from the individual frequencies are overlaid. All three curves intersect at the true gel point, where the tan(δ) becomes independent of frequency. Interestingly, the true gel point does not occur at exactly tan(δ) =1 with this approach and can be higher or lower than 1 depending on the thermoset's formulation. In Figure 10b, the

gel point for the epoxy thermoset used in this study is observed to occur at tan(δ) = 1.3. Our results highlight the advantages of using multi-wave analysis for gel point determination. Compared to the conventional approach, the ability to simultaneously collect all three frequencies in a single experiment represents a significant reduction in experiment time and can be an extremely valuable tool to characterize thermoset curing.

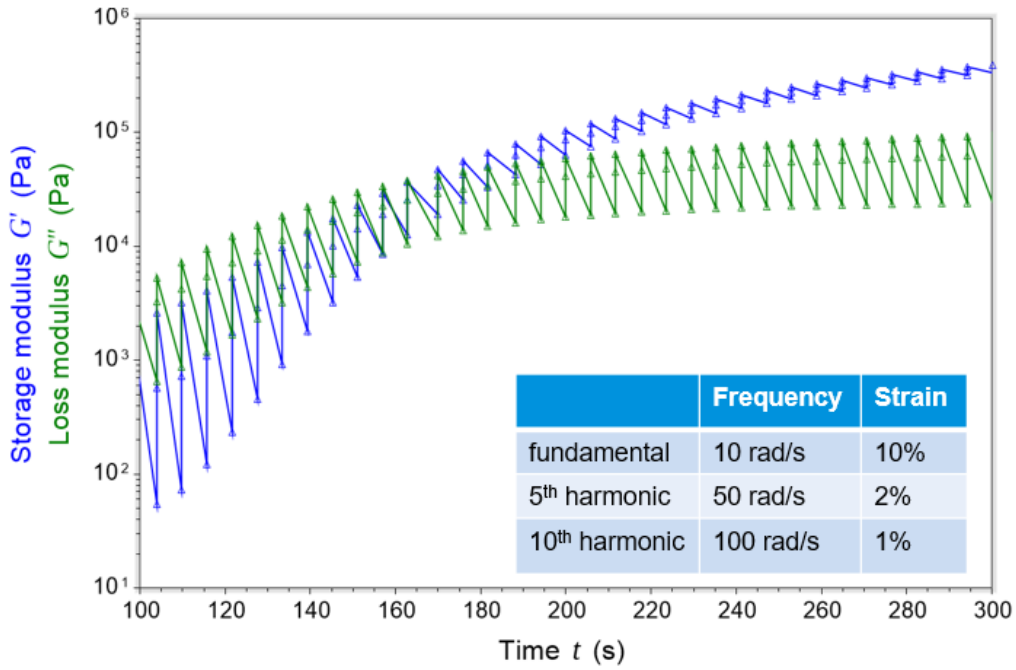

Figure 9. Raw data from multi-wave test at 80°C to monitor epoxy curing. The fundamental frequency was set at 10 rad/s, higher harmonic frequencies were programmed at 50 rad/s and 100 rad/s.

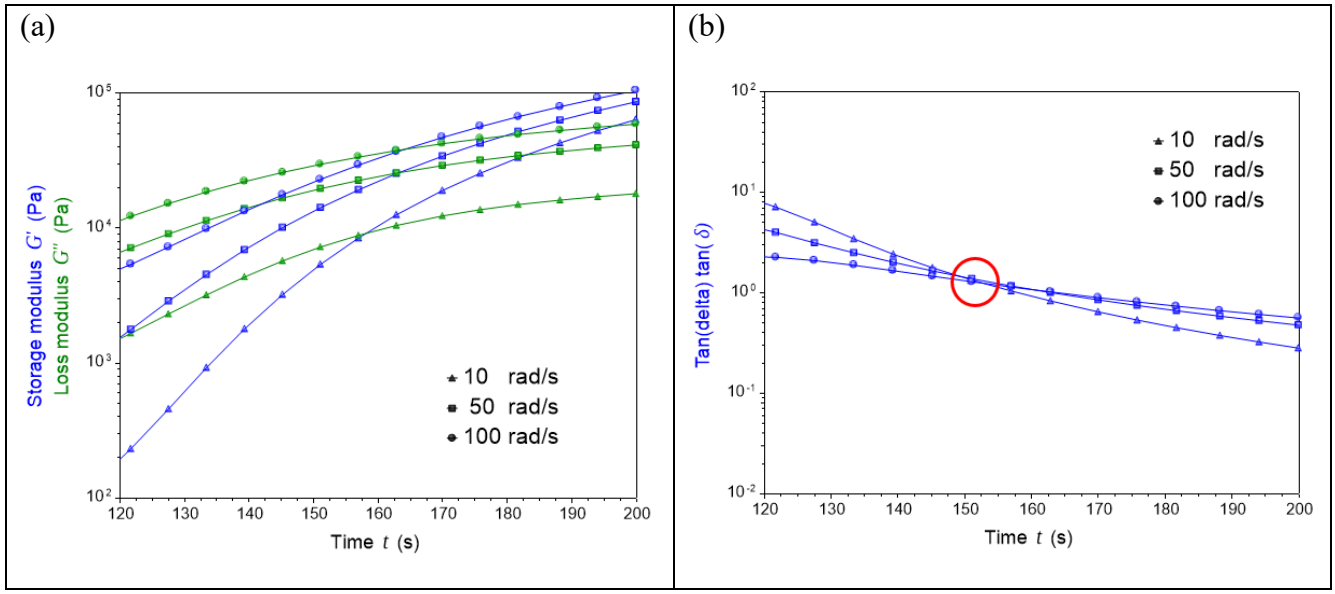

Figure 10 Overlay of individual frequency data from Multi-wave experiment shown in Figure 9. Plot of the tan(δ) signal clearly identifies the "true gel point" during the curing reaction.

3.3.2 Quantifying Gel Kinetics from Rheological Measurements

We conclude our study by briefly commenting on calculation of gel kinetics parameters using rheological data. The dependence of gel time on cure temperature can be described using an empirical Arrhenius model shown in equation (1) [16,22]:

$$t_{gel} = t_{gel}^{\infty} \exp\left(\frac{\Delta Eg}{RT}\right) \tag{1}$$

Where t_{gel} is the gelation time, Eg is the gel activation energy, t_{gel}^{∞} is the gelation constant, R is the gas constant and T is the isothermal cure temperature. Figure 11 shows the results of epoxy curing at 4 different temperatures ranging from 50 °C to 100 °C. At each temperature, the gelation time, t_{gel}, was determined as the modulus crossover point. From this data, a plot of t_{gel} versus 1/T (Figure 12) was used to calculate the gelation activation energy, Eg, and gel time constant, t_{gel}^{∞}. For the epoxy sample we test in this paper, we determine a gelation activation energy of 61.7 kJ/mol. With this information, one can predict the time to reach the gel point at any isothermal temperature within the experimental temperature range.

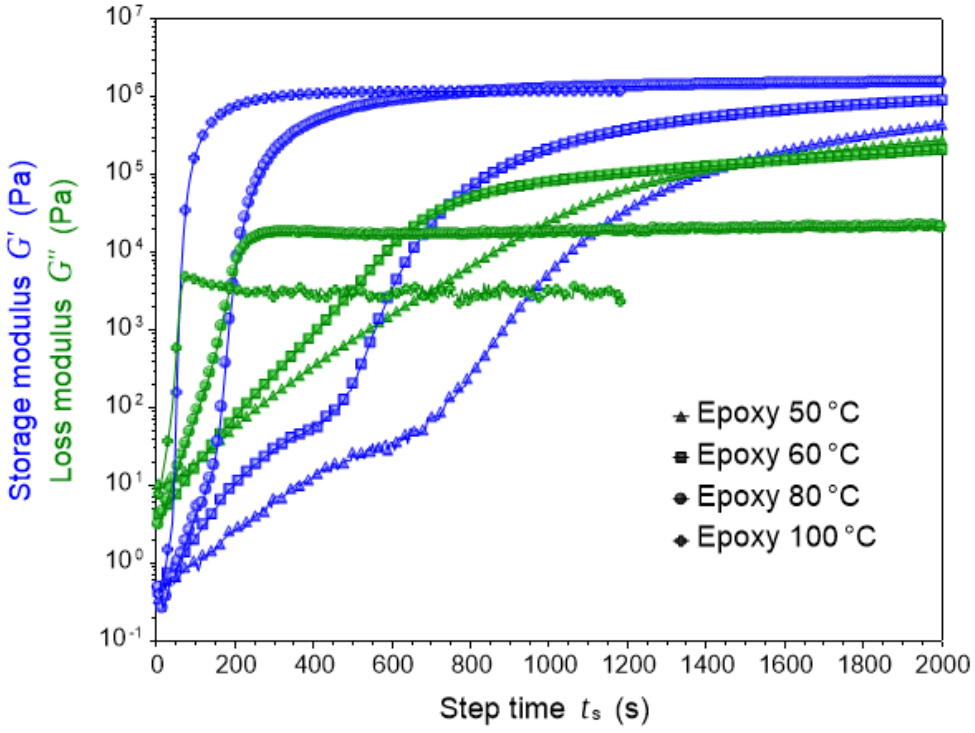

Figure 11. Overlay of epoxy curing at different isothermal temperatures: 50°C, 60°C, 80°C and 100°C. The gel point, t_{gel}, was identified as the G'/G" crossover at each temperature.

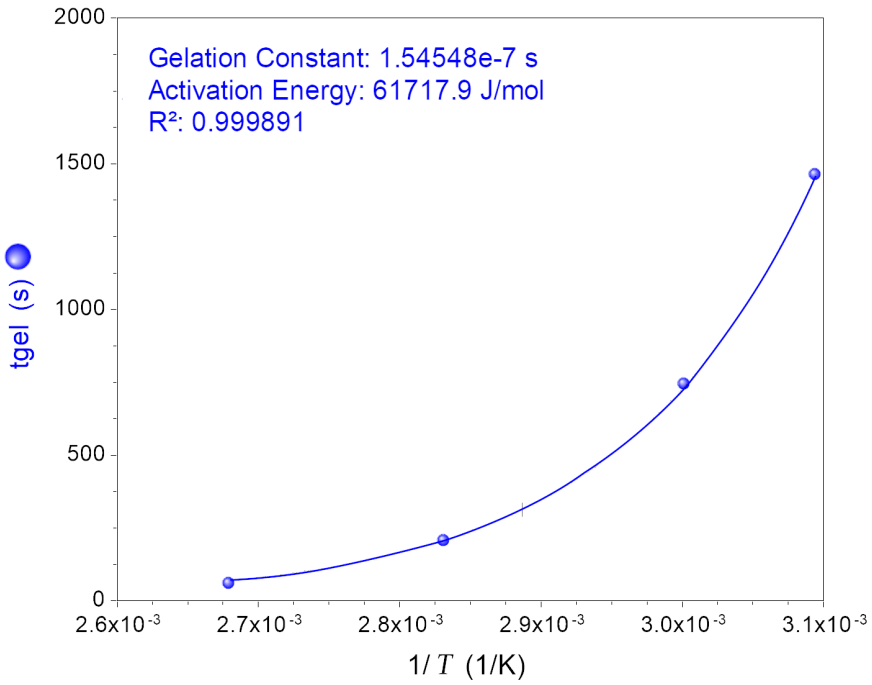

Figure 12. Arrhenius plot to determine activation energy from the data presented in Figure 11.

4. CONCLUSIONS

Rheology is a powerful technique for characterizing thermoset curing and can reveal information about critical parameters such as minimum viscosity, gelation time, and final cured modulus. Compared with standard rheology tests, the cure-induced changes in rheological parameters are rapid and dramatic, posing unique challenges when designing test methods that can track the entire curing process. In this paper, we highlighted key test parameters that warrant attention during method development and play an important role in achieving good results.

The single most important parameter in a curing experiment is the oscillation strain. The strain must be within the sample's linear viscoelastic region throughout the test, should ensure a good signal-to-noise ratio at the beginning of a curing, and should not overload the instrument torque once sample is fully cured to a rigid solid. Two approaches for dynamically adjusting the oscillation strain during curing experiment were introduced viz., Non-iterative sampling and Auto-strain control. In addition, we also discussed the use of axial force control which permits an accurate measurement of sample shrinkage during curing.

We introduced the multi-wave rheological test method for the measurement of true gel point. This method allows simultaneous measurements at multiple frequencies for unambiguous determination of the gel point in a single test. Multi-wave tests significantly shorten the experimental time needed for true gel point measurement and minimizes potential errors arising from preparing and loading multiple samples. Finally, we concluded with the gelation activation energy calculation from gel point data and discussed its relevance for the process engineer

looking to optimize cure times. While the data presented in this study focus on an epoxy curing material, the principles outlined here are relevant for all materials that undergo a gel transition, including all classes of thermosets, hydrogels, UV-curable adhesives, and more. The control techniques and practical templates detailed here can serve as a useful blueprint for engineers and scientists looking to characterize the rheological behavior of curing systems.

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