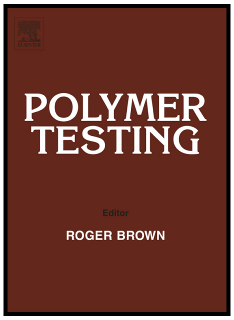

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Test Method

Evaluation of Cure Shrinkage Measurement Techniques for Thermosetting Resins

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Abstract

Resin chemical shrinkage dictates the surface integrity and the roughness of a composite structure. Thus, to minimize surface failures and to produce a good surface quality it is a requisite to be able to measure and track resin shrinkage during the cure process. This manuscript investigates and evaluates the measuring and monitoring of real-time resin shrinkage using a rheometer, a helium-based pycnometer and a thermo-mechanical analyzer (TMA) for ambient curing UP and epoxy resins. Shrinkage readings obtained from the newly developed robust technique with the rheometer concur well with readings from the traditional pycnometric method. They also coincide within the accepted literature values of 7-10% and 3.5-4.5% for the UP and epoxy systems, respectively. Shrinkage measurements during post-cure were effectively carried out at an elevated temperature, suggesting that the methodology provided can be applied to non-ambient curing systems. The TMA was found to be unsuccessful in measuring shrinkage reliably.

Keywords: Chemical shrinkage; Cure behavior; Pycnometer; Rheometer; Thermal analysis; Thermosetting resins

1 Introduction

1.1 Chemical shrinkage during cure

A thermoset resin is transformed into a rigid intractable solid (plastic or rubber) through an energy and/or catalyst activated curing process. The curing process is commonly described

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via three distinct regions (*Fig 1*) [1]. In Region I, the resin is uncured and behaves as a viscous fluid. The liquid mobile monomer molecules can be considered as chemical entities that are discrete with respect to one another. They are said to each occupy a unit volume that is dictated by their Van der Waals volume and thermal energy (*Fig 2*) [2].

Region II denotes the curing stage of the resin. In this exothermic process, the monomer molecules first undergo chain formation and linear growth through branching (polymerization) [3]. Then the resulting molecular chains form cross-links so that a large rigid three-dimensional molecular network is formed.

Polymerization and additional bonding via branching lead to a reduction in the degrees of freedom to store thermal energy. This implies that the previously mobile and discrete monomers become constrained and closely-packed polymer units (*Fig 2*). Furthermore, the Van der Waal bonds between molecules convert to stronger yet shorter covalent bonds. A significant increase in the stiffness (chemical hardening) and reduction in specific volume (chemical shrinkage) of the system are then observed.

If the system is cured at an elevated temperature or experiences a significant exothermal reaction and, hence, requires additional cooling, extra shrinkage (thermal shrinkage) may be observed. This, however, depends on the trade-off [4] between i) the thermal expansion of the resin during the elevated temperature post cure, ii) contraction of the more fully cured material and iii) contraction of the resin during the cooling step.

For this study, to allow linear shrinkage measurement without compressing the initially liquid resin, resin chemical shrinkage is assumed to occur at the point of resin gelation, and is assumed to be completed once the resin is fully cured or diffusion limitations restrict further development. In reality, however, as shrinkage is directly proportional to the degree of cure [5-7], it occurs when conversion from Van der Waals to covalent bonds first begins. Region III marks the end of the curing process.

Cure shrinkage is notorious for its potentially serious consequences, depending on the application of the material [8]. Thermosets are typically used in combination with stiffer reinforcements. Hence, the shrinkage is constrained and residual stresses are formed in the structure. These stresses can result in early product failure due to warpage, void formation, stress cracking, delamination and poor fiber-matrix adhesion [3, 8-10]. Experimental work based on statistically robust test methods have further indicated that the surface roughness of the end product is a function of textile architecture and matrix shrinkage [10, 11].

This research looks at several methods for measuring resin cure shrinkage and isolates a selection of commonly used methods within the composites industry. A new method using rheometry is also detailed in this study and is compared to the current industry standard methods.

1.2 Approaches to measure chemical shrinkage

A variety of techniques have been applied to measure the volumetric change or dimensional change of a cross-linking resin. Hence, it can be said that there are two general approaches to measuring resin shrinkage: volume dilatometry and linear (axial) shrinkage measurement.

Volume dilatometry is based on the measurement of volume change and, for many years, mercury-based dilatometers were the only means to measure shrinkage [6-8, 12-14]. In this instrument, the body of the capillary dilatometer is first filled with the uncured resin and then surrounded with an immiscible fluid (often water [15] or mercury) which extends into a graduated capillary. As the volume of the resin changes, the level of fluid in the capillary also changes; and this change in height is then used to calculate volumetric change or shrinkage.

The potential hazard with the toxic mercury vapor, limitation of using ambient curing systems and the sensitivity of the apparatus to even small temperature changes led to the use of pycnometers [16]. Gas based pycnometers use Boyle’s law to measure volume [8, 17, 18]. This method of measuring shrinkage offered similar accuracy and was less labor intensive [12]. However, it remains unsupportive of in-situ shrinkage monitoring under non-ambient and non-isothermal conditions; that is, it only enables the determination of final shrinkage.

Other methods of measuring volume change have employed the use of strain gauges [19, 20], linometers [21], density gradient columns [4] and even the straightforward principle of buoyancy [22].

Linear shrinkage measurement, on the other hand, involves measuring dimensional changes of the mixed resin sample and making assumptions, such as plane strain conditions [10] and isotropic contraction [23], to derive a final value for volumetric shrinkage.

A modern rheometer can be configured to measure linear shrinkage and investigate the rheological behavior of the resin [10, 24]. Torque or strain controlled tests can be performed to not only determine the point of gelation but also to monitor dimensional changes of the resin as it cures.

Thermo-mechanical analyzers (TMA's) have been previously used to measure linear dimensional changes by monitoring resin thickness as a sample cures under applied loads and isothermal conditions or specified temperature ramps [12].

Laser interferometry [25], optical fibers and dynamic-mechanical analyzers (DMA's) [8, 26] have also been used to measure linear shrinkage to a reasonable degree of accuracy.

This paper investigates the measurement of resin shrinkage using a rheometer, a helium-based pycnometer and a TMA. A Differential Scanning Calorimeter (DSC) was employed to measure the degree of cure (DoC) of the resin, thus enabling the comparison of real-time resin shrinkage from the three methods with respect to the DoC. A thorough comparison of the results from the three methods is performed to evaluate the accuracy and precision and other advantages or disadvantages of the general methodology. The most effective method of measuring shrinkage is then identified.

2 Methodology

2.1 Material: resin selection

Resin systems that were considered for this study are presented in *Table 1*. Ambient curing systems were desirable so that shrinkage could be monitored throughout the curing process in a pycnometer. The unsaturated polyester resin (UP) system was obtained from Reichhold Norpol and epoxy systems from Gurit UK Ltd.

An attractive resin system for this study was one which cures at ambient temperature (~25°C), has a fairly short curing time, low-to-moderate peak exotherm temperatures (<70°C) and has a slow initial cure rate. To select the best suited systems, the temperature profile of each resin system was tracked throughout the three-region curing process using DSC (*Fig 3)*.

It is observed that the epoxy systems have a low initial cure rate, but take an extended time to reach peak exotherm and to completely cure. The UP systems reach peak exotherm quickly, but have a high initial cure rate. Furthermore, the UP systems reach much higher temperatures during cure than the epoxies.

Fig 3 enables us to categorize the resin systems into two distinct classes: Class I ideal for TMA and rheometric analyses and Class II for pycnometric analyses.

Class I resin display large variation in temperature in a small amount of time; these are not suitable for pycnometric analysis as volume measurements using pycnometers should be made under isothermal conditions.

Class II consists of resins that are ideal for pycnometric analysis as they have a slow initial cure rate, hence volume changes can be tracked to better resolution. Furthermore, as these resin systems display lower peak temperatures, volume readings are less likely to be skewed from effects of thermal shrinkage.

For this investigation, UP Type 420-100 (with 0.25wt% NL 49P accelerator and 1wt% Butanox M50 initiator) and Ampreg 21 epoxy resin (with 33wt% Ampreg 21 slow hardener) were selected. The mixtures were mixed thoroughly at 25°C, noting the dependency of resin rheology (including shrinkage) on the resin to catalyst ratio and the temperature during cure.

These two systems were selected as they best met the criteria. Additionally, resins from the two separate classes allow a true cross-comparative study of the accuracy of the various shrinkage measurement techniques.

2.2 Experimental

2.2.1 Rheometer

Linear shrinkage measurements and rheometric analyses of the resins were conducted using a Bohlin Instruments C-VOR 200 Rheometer. The experimental setup utilized is presented in *Fig 4*. The test employs R20mm smooth aluminum parallel plates in oscillation mode. The base plate is fixed rigidly whereas the top plate can move vertically, thus enabling the application of a compressive normal force F_z, and the transmission of a torque or rotary frequency f, essentially permitting the transfer of shear strain to the resin sample.

To determine the region of linear viscoelastic response (LVR) of the resin, an amplitude sweep in oscillation mode is first performed. The sweep is conducted in an isothermal condition of 25 ± 0.2°C under strain control, as LVR is a strain related function. Thus, the VR of the sample is measured over a range of specified angular strain amplitudes (0.003% to 30%) at a constant frequency of 0.2Hz. The gap is set constant at 0.5mm.

In the linear region so determined (where material properties are constant), a strain-controlled frequency sweep in oscillation mode is then performed to study the viscoelastic properties of the resin as a function of frequency. This is done by measuring the VR of the resin over a range of specified frequencies (0.2Hz to 30Hz) at a constant angular strain of 0.003%. The gap is set at 0.5mm.

The amplitude and frequency sweeps indicate the range of strains and frequencies that keep the resin in the linear region. This enables the parameters to be set for the rest of the experiment. The main test procedure involves running the rheometer in three segments:

- Segment I - Pre-Gelation
- Segment II - Post-Gelation
- Segment III - Post-Curing

In Segment I, a single-frequency stress-controlled test is conducted at 0.2Hz in oscillation mode with the gap between the plates kept constant at 0.5mm and the strain set at 15%. As the resin is in a liquid state no normal force is applied.

At the point of gelation, the test is moved into Segment II. For this study, the crossover point of the elastic modulus, G', and the viscous modulus, G", is taken as the liquid-solid transition point for the resin as G' is now comparable to G''.

In Segment II, the resin is at the liquid-solid transition point. A single frequency stress-controlled test is conducted at 30Hz in oscillation mode. A torque of 500µNm and a constant compressive normal force of 0.1N are applied under isothermal ambient conditions. The equipment is set to compensate the gap to keep the compressive normal force constant at 0.1N. The actual gap is plotted against time to monitor linear dimensional change during cure. By virtue of the gelled resin and low normal force applied, no material was forced out from between the plates so giving a false measurement.

Once the gap stops changing, the rheometer is run in Segment III. A post-cure analysis of the resin is performed at 55°C ± 0.2°C for 6 hours using an Extended Temperature Control (ETC) Oven. All other conditions from Segment II remain in effect, while the actual gap is monitored. After 6 hours, the gap is tracked again at ambient temperature to eliminate the effect of thermal shrinkage and obtain true chemical shrinkage.

Finally, the variation of the gap is used to compute resin chemical shrinkage ε_V using Equation 1, where h_0 is the initial gap and h is the actual gap. This equation has been derived by M. Haider et al. [10] assuming that the resin sample in-plane strains are zero. This assumption can be confirmed through visual inspection of the sample in the plates as the strong adhesion between the resin and the plates prevent any in-plane motion. A further assumption made is that the resin is incompressible. A negative sign for ε_V implies a volumetric contraction or shrinkage.

$$\varepsilon_V = \left(1+\frac{1}{3}\left(\frac{h-h_0}{h_0}\right)\right)^3 - 1 \qquad \mathbf{1}$$

2.2.2 Pycnometer

A calibrated Micromeritics AccuPyc 1330 Gas Pycnometer is used to measure and monitor the volume of the resin sample as it cures at ambient temperature. This instrument works by measuring the amount of displaced gas (*Fig 5*). The pressures observed upon filling the specimen chamber and then evacuating it into a second empty expansion chamber allows the computation of the sample solid phase volume. The final volume reading is an average of five systematic readings from five purges and runs.

For this test, first an empty disposable aluminium cup is placed in the specimen chamber and its volume V_c is measured. Then, approximately 4cm^3 of the uncured resin is poured into the cup and the volume of the uncured resin V_i is obtained by the subtraction of V_c from the total volume. Measurements of the sample volume V_f are then made at fairly regular intervals, under ambient conditions, as the resin cures (Segment I).

Post-cure (Segment III) is conducted at 55°C for 6 hours by placing the resin filled cup into an oven. Due to the limitation of the pycnometer to ambient volume measurements, only a final volume reading is measured upon the completion of Segment III.

To determine the resin chemical shrinkage ε_V at time t during the curing process, Equation 2 is used. Again, a negative sign for ε_V implies a volumetric contraction or shrinkage.

$$\varepsilon_V = \left(1-\frac{V_f}{V_i}\right) \qquad \mathbf{2}$$

2.2.3 Thermo-mechanical Analyzer (TMA)

A TA Instruments TMA Q400 was also used to determine the linear shrinkage of the UP and epoxy resin systems by a method adopted from H. Yu et al. [12]. The test stage used is presented in *Fig 6*. Disposable microscope slides (10mm by 10mm square) are placed on the stage shield and their thickness T is measured at 25°C. 0.005cm^3 of the mixed resin is then placed on the bottom microscope slide and covered with the top slide. A layer of resin approximately 20µm thick is formed by rubbing the two slides together. The initial thickness of the resin layer h_0 is determined by measuring the total thickness of the sandwiched sample. Hence, the measurement of the dimension change (h_0-h) or the new resin thickness h is conducted under isothermal cure at 25°C until curing is complete. A very low constant compressive load of 0.02N is also applied. The chemical shrinkage of the resin at time t can be calculated using Equation 1.

2.2.4 Differential Scanning Calorimeter (DSC)

A TA Instruments DSC Q10 was used to measure the degree of cure (DoC) of the resin system at regular intervals during the curing process. Approximately 20mg of the mixed resin was tested in a dynamic analysis from 20°C to 200°C with a rate of 10°C/min under scanning temperature mode.

Universal Analysis software was used to calculate the specific heat enthalpy of reaction Δh_t at time t of the curing process for each sample. For this, the onset points on each graph are determined by the software and manually accepted as limits to perform numerical integration, assuming a linear or curve approximation. Equation 3 is then used to determine the fraction of the resin cured (DoC) in the DSC.

$$DoC = \left(1 - \frac{\Delta h_t}{\Delta h_0}\right) \quad \mathbf{3}$$

where, Δh_t is the specific heat enthalpy at time t during resin cure and Δh_0 is the reference specific heat enthalpy at t = 0min

3 Results and Discussion

3.1 Unsaturated Polyester Resin

3.1.1 Rheometer

Initial gel-point determination tests and Segment I tests for UP on the rheometer revealed a family of G’ and G’’ characteristic curves where the time to gelation is given by the G’ and G” crossover point.

The time to gelation and associated values of G’ (and G’’) over multiple runs are shown in *Table 2*. The average time to gelation for this UP system is evaluated to be 1733s (28.9min) with a range of about 150s (2.5min). The small range highlights the precision of gel-point measurement for this UP system using a rheometer, noting that there will be an inherent difference in the values as samples are not put on the aluminium plates at the same time after resin mixing. It is also observed that G’ and G’’ crossover at almost the same value each time (~14.7Pa), thus further illustrating the reliability of the method employed.

Segment II shows the progression of resin shrinkage with increasing DoC as measured by the change in gap between the parallel plates. Three repeat tests (two shown in *Fig 7*) were run for about 20 hours in Segment II after which no change in gap was detected. The three tests produced results that are very similar in nature and display a final gap size of 0.453mm ± 0.001mm. At the end of Segment II, the UP system displays chemical shrinkage of 9.17%, which falls within the literature value of 7-10% [9, 10].

There is noticeable fluctuation in the gap size early on during Test 2 and at about 630mins in Test 3 (*Fig 8*). This instability is probably due to anisotropic volume contraction of the resin or perhaps external disturbances during the experiment. However, it is proposed that these do not affect the final shrinkage value as Segment II is run under gap compensation mode with a constant compressive load.

A post-cure regime (Segment III) is employed with Test 3 only. When the ETC oven is placed over the sample and the sample is heated, an initial disturbance region is observed in which the resin expands due to heat and the temperature of the resin (detected by the thermocouple under the parallel plates) is changing from ambient (25 ± 0.2°C) to the required 55 ± 0.2°C after an overshoot to about 57°C. Once the change in gap becomes gradual and approaches zero, the test has officially entered Segment III. After 6 hours, the ETC oven is removed and, again, a disturbance region is created in which the gap drastically starts to fall due to thermal contraction. Once the resin reaches a stable ambient temperature and the gap remains constant at the final value.

For this UP resin system, a 0.001mm reduction in gap is observed after a post-cure analysis, moderating the final gap to 0.453mm. This implies that 9.10% is the final chemical shrinkage of the UP resin as measured with the rheometer. The ability to monitor shrinkage at elevated temperatures using the rheometer suggests the ease with which energy and heat activated curing systems can be employed.

3.1.2 Pycnometer

The pycnometer also enabled easy determination of chemical shrinkage for the UP resin. Calibration of the pycnometer and initial error determination tests performed suggested a calibration error of only 0.003%, thus ensuring high precision volume measurements.

Shrinkage determination tests produced results as presented in *Fig 9*. Segment Ia and Segment Ib are of the resin volume being measured as it is curing at ambient temperature. Segment III measures the volume of the resin sample after post-curing at 55°C.

Curing the UP system under ambient conditions results in 8.45% shrinkage, with a further post-cure increasing the shrinkage to 9.35%. These values of shrinkage concur with the literature value of 7-10% [9, 10] and with the result from the rheometric analysis of 9.10%.

One aspect that begs discussion is the sudden change in the rate of volume change observed from Segment Ia to Segment Ib. It is even more interesting as this phenomenon is not observed in the rheometer tests – perhaps because the rheometer measures shrinkage post-gelation. There is no ready explanation for this observation. Further research and repeat tests should be conducted to analyze change in resin properties that might be causing this or to identify apparatus or methodology errors.

A possible explanation is that the pycnometer measures the volume of the sample using Boyle's Law which is applicable when the temperature is constant; however, during the exothermic curing reaction, the resin emits heat and alters the temperature. Segment Ib begins at 102mins (*Fig 9*) which is evidently very close to the time at which the exotherm temperature of this UP system returns to constant ambient temperature (*Fig 3*). Thus, perhaps Segment Ia denotes the region where the temperature of the resin system is constantly changing, whereas in Segment Ib the temperature is constant at ambient temperature.

Another important point to note is that the presence of or formation of voids (due to air bubbles in the sample itself or due to the shrinkage of the resin) will lead to unreliable volume data. The cup used for pycnometric analysis is made from aluminum which is a good conductor and dissipater of heat. Thus, bubbling of the resin, if it reaches high temperatures due to the internal exotherm in the curing stage, is avoided.

A release agent was applied to the internal sides of the cup so that the resin would not stick to the walls, hence shrinkage will not result in void formation. Simultaneous curing of the sample in a polypropylene tri-cornered beaker showed that air-bubbles or voids were not formed.

3.1.3 Thermo-mechanical Analyzer

Experiments with the TMA were not successful, highlighting the inability of thermo-mechanical analysis to measure or monitor cure shrinkage of resins reliably. The issue was not only in measuring or tracking the dimensional change of the resin sample, but even greater difficulty was faced in setting up the experiment.

Firstly, it was extremely difficult to pour 0.005cm^3 of resin onto the microscope slides. Forming a 20μm layer was even more difficult; when the top slide was placed on the mixed resin, it would simply squeeze the resin layer out. Increasing the volume of resin made no difference to the thickness of the layer formed.

Tests were continued with a 2.5μm resin layer, rather than the manufacturer prescribed 5-10mm sample size for adequate resolution on the TMA. Although being a state-of-the-art apparatus with high accuracy where the temperature is kept constant at 25ºC ± 0.025ºC and the force is kept stable at exactly 0.02N, the resin layer was too small for the TMA to accurately track dimensional changes. After a 5-hour analysis, the TMA reported a dimensional change of 0.8μm which implies a mammoth volumetric shrinkage of 29%. This implies that the TMA is not truly measuring shrinkage and that the liquid resin was being pressed out of the slides due to the weight of the top slide and the force being applied. Noting the failure of this methodology, the epoxy resin was not tested with TMA.

A more effective methodology for shrinkage measurement using a TMA needs to be developed, for instance by measuring linear dimensional change of a curing resin system in a cup. A flaw in the current methodology is that a load is being applied on the resin layer pre-gelation when the resin is still liquid. Perhaps, post-gelation tests should be conducted, however, thought needs to be given to gel-point determination using a TMA.

3.1.4 Differential Scanning Calorimeter

DSC analysis of the UP system revealed that curing the resin under ambient conditions only cured it to about 85%. A post-cure regime was required to reduce the heat evolved during the temperature scan in the DSC to 2.53J/g and, hence, the DoC to 99%.

This provides an explanation as to why the pycnometer initially displayed 8.45% shrinkage and after post-curing displayed 9.35% shrinkage. As post-curing the resin makes it fully cured and as shrinkage is proportional to DoC, we can show further confidence in the accuracy of the pycnometric analysis for shrinkage measurement. It can also be concluded that a post-cure regime is essential for the UP system.

Fig 10 shows the heat evolved from the resin samples under dynamic analysis over 24 hours and the DoC of the resin over time. As expected, the nature of the two graphs is very similar. It is also noted that linear and curved approximations gave very similar results implying that the initial and final heat flow at 20ºC and 200ºC, respectively, were almost the same for all runs.

To further assess the reliability of the results, the relationship between shrinkage of the resin and the degree of cure was determined (*Fig 11*). As previously mentioned, volume change during cure is directly proportional to the degree of polymerization (DoC).

The study confirmed the current speculation; for the rheometer, $R^2 = 0.99$ and for the pycnometer, $R^2 = 0.98$, both of which imply very strong positive correlation. This again confirms the reliability of the methodology employed for measuring resin shrinkage using both the rheometer and pycnometer. Furthermore, the gradient of the curves for the rheometer and pycnometer are similar, implying a good match of the curing process.

3.2 Epoxy Resin

3.2.1 Rheometer

Initial gel-point determination and Segment I tests with the epoxy system were inconclusive as G’ and G’’ would not crossover, even for increased sample sizes during resin mixing and delayed placement of the sample on the aluminium plates. *Fig 12* shows this phenomenon.

Therefore, the rheometer test method was modified by using tack tests that were performed simultaneously with the resin sample in Segment I. When tack tests showed that the resin had gelled and was no longer in a liquid state, the rheometer was run in Segment II. After 20 hours in Segment II, a post-cure study (Segment III) was conducted. *Fig 13* presents the percentage volume change of the resin in Segment II and III.

The rheometer tests were repeated three times with the volume shrinkage at the end of Segment II being 2.8%, 3.2% and 3.7%. The variation in the values is mainly due to the slightly different times that the samples were moved into Segment II using subjective hand tack tests for gelation. Since a large percentage of shrinkage occurs early on (close to the gel point), moving into Segment II even a few minutes late can mean that a significant percentage of shrinkage is not accounted for.

Multiple tests with better tack test facilities can significantly reduce the variation in the values, giving us a more precise value of shrinkage. However, as the shrinkage measured in Test 3 (3.7%) lies in the range of the expected value of 3.5 - 4.5% [27], some confidence can be shown in the current methodology employed.

For a Segment III analysis of the epoxy resin, the ETC oven is placed over the sample. The resulting volume change profile observed (*Fig 13*) is similar to that observed for the UP system in *Fig 8*. Unstable regions are observed where there is a transition of temperature from ambient to 55°C or vice-versa.

For this epoxy resin system, no change in shrinkage (or gap) was observed after a post-cure analysis. This implies that 3.7% is the final chemical shrinkage of the epoxy resin as measured with the rheometer.

3.2.2 Pycnometer

Shrinkage determination tests produced results as presented in *Fig 14*. For this graph, in Segment I the resin volume is being measured as the resin cures at ambient temperature and in Segment III the resin volume is measured after post-curing.

Curing the epoxy resin under ambient conditions results in 4.10% shrinkage. A further post-cure analysis shows that the shrinkage remains at 4.10%. Not only does this value of shrinkage coincide with the literature value of 3.5-4.5% [27], it also correlates well with the rheometric analysis as the rheometer also suggested that post-curing the epoxy resin does not change the shrinkage. Hence, we can show confidence in the method we have employed using the pycnometer to assess shrinkage of the resin and re-emphasise the suggestion that the method employed using the rheometer is effective, but a new technique is required to pin-point the exact gel-point to start measuring dimensional change at the right time for accurate shrinkage measurement.

It is worth noting that pycnometer results for the epoxy system do not show a different rate of volume shrinkage before and after the exothermic stage, as the UP system does (Segment Ia and Ib). This may be because the epoxy system reaches a lower exothermic range of temperatures over a much longer period which does not affect the readings.

3.2.3 Differential Scanning Calorimeter

DSC analysis revealed that curing the resin under ambient conditions only cured it to about 83%. A post-cure regime was required to reduce the heat evolved during the temperature scan in the DSC to 1.8J/g and, hence, the DoC to 99.5%.

It was observed for the UP resin that post-cure changed the DoC from 85% to 99% and the shrinkage proportionally from 8.45% to 9.4%. Interestingly, although post-cure has a significant effect on the DoC of the epoxy system, both the pycnometer and rheometer showed no change in shrinkage after post-cure. This seems to contradict the current understanding that shrinkage is directly proportional to DoC.

A possible explanation for this is that shrinkage is not observed after vitrification [7]. Hence, although the material wants to contract as Van der Waals bonds are replaced by covalent bonds, the rigid glassy material cannot contract in the time scale of the curing reaction. Furthermore, the epoxy system is very dependent on the volume of resin mixed as compared to the polyester resin. The 20mg samples in the DSC might have required a post-cure because the sample was too small to produce a large exotherm to accelerate the process of cross-linking and polymerizing, whereas the sample used in the pycnometer of 4.14cm^3 and the rheometer of 0.63cm^3 is large enough to produce an exotherm that assists the sample in cross-linking and polymerizing. Further research could be conducted to investigate the dependence of shrinkage on resin volume.

To further assess the reliability of the results a cross-study was done, analysing how the shrinkage of the resin changed with the DoC.

The study concurred with the current speculation and it was again observed that the shrinkage for the epoxy system was directly proportional to DoC of the resin. This further confirms the reliability of the methodology employed for measuring resin shrinkage using both the rheometer and pycnometer.

3.3 Analysis Summary

Table 3 summarizes the results from all the analyses performed on the UP and epoxy system. As the shrinkage values for the pycnometer and rheometer are very similar and fall between the accepted range of literature values, confidence can be shown on the apparatus and methodology employed for the measurement of shrinkage. The TMA could not be used to determine shrinkage.

4 Conclusions

From the comprehensive investigation of the measurement of resin shrinkage utilizing different instruments, it can be firstly concluded that the rheometer methodology outlined provides a means of robust analysis of not only resin shrinkage but also the rheological properties of the resin throughout the curing process. For some resins it accurately determines the point of gelation as well. Some work needs to be done in developing a means of determining the gel-point of resins for which G’ and G’’ do not crossover during the curing process. However, it is to be noted that a rheometer measures only post-gelation shrinkage.

Secondly, the pycnometer can also be utilized for quick and high precision measurements of shrinkage during cure. Although monitoring volume change is tedious with this instrument, it is proposed that the pycnometer can be used to perform one-off quality checks to compare with the rheometric measurements, and the rheometer can be widely used to monitor shrinkage and rheological properties for investigative and development purposes.

Finally, it can be concluded that the TMA cannot be used to accurately measure resin shrinkage for liquid resin systems using the current methodology.

Although this investigation employs ambient curing systems, the methodology provided can be easily applied to non-ambient curing systems. The post-cure study at an elevated temperature is evidence of this.

Further research should be conducted to understand the effect of curing temperature and history and resin volume on the chemical shrinkage of the resin. It is already known that elevated temperature curing requires the subtraction of thermal expansion/contraction, while resin volume affects curing time, DoC and final shrinkage due to different levels of internal exotherm generated. Specific research could also look at the effect of change of resin thermal expansion coefficient and effect of interfacial contact stress between the disks in the rheometer and the resin on the volumetric shrinkage of the resin.

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Figure Captions

Fig 1 [1]: Three distinct regions in which the physical properties of resin change throughout the cure process. v_i and v_f are the specific volume of the system at gelation and 100% cure, respectively.

Fig 2 [1]: Schematic of unit cell contraction during the cure process due to reduction of thermal energy and conversion of Van der Waal to covalent bonds.

Fig 3: Curing temperature curves for the resin systems

Fig 4 [10]: Test setup for linear shrinkage measurement using a rheometer

Fig 5: Schematic of a pycnometer that uses a gas displacement technique

Fig 6: Schematic diagram of the test setup for TMA analysis

Fig 7: Segment II rheometry test results of UP resin

Fig 8: Test 3 - a complete Segment II and III run in the rheometer for UP resin

Fig 9: Pycnometer test results for UP resin

Fig 10: DSC analysis results upon ambient and post-cure for UP

Fig 11: Shrinkage and DoC are found to be directly proportional for UP

Fig 12: Gel-point determinations tests were inconclusive for the epoxy system

Fig 13: Rheometry Test 3 results for the epoxy system

Fig 14: Pycnometer test results for Ampreg 21 Epoxy

Tables

Table 1: Resin systems considered for investigation

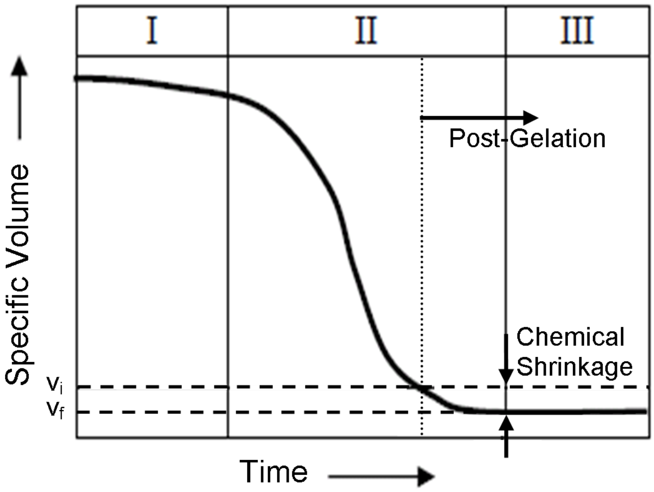
Table 2: Gelation and shrinkage study of UP Reichhold Norpol Type 420-100

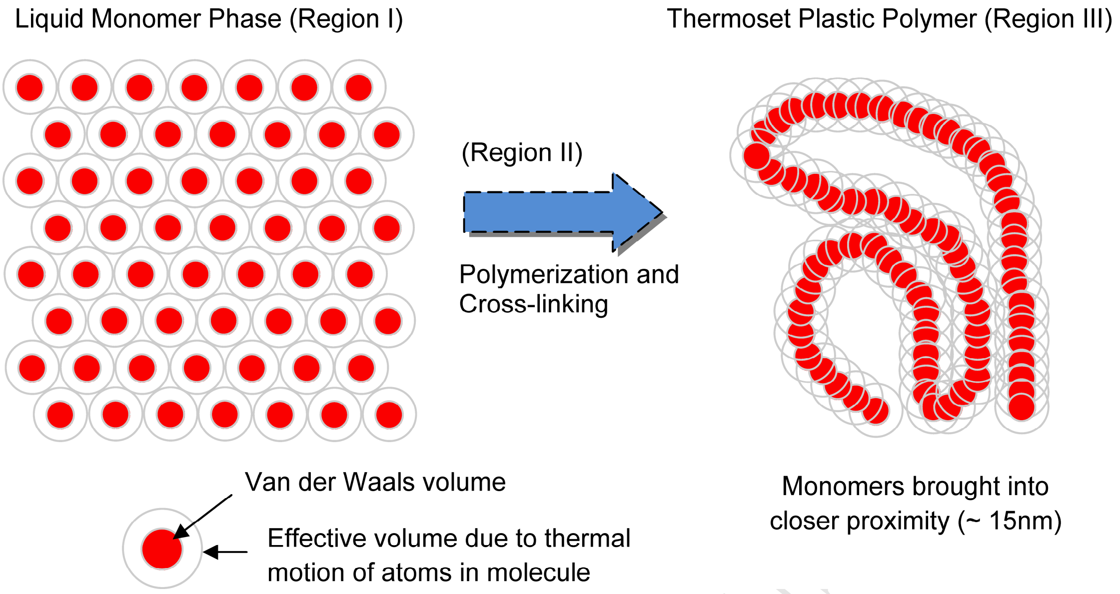
Table 3: Summary of results for shrinkage analysis

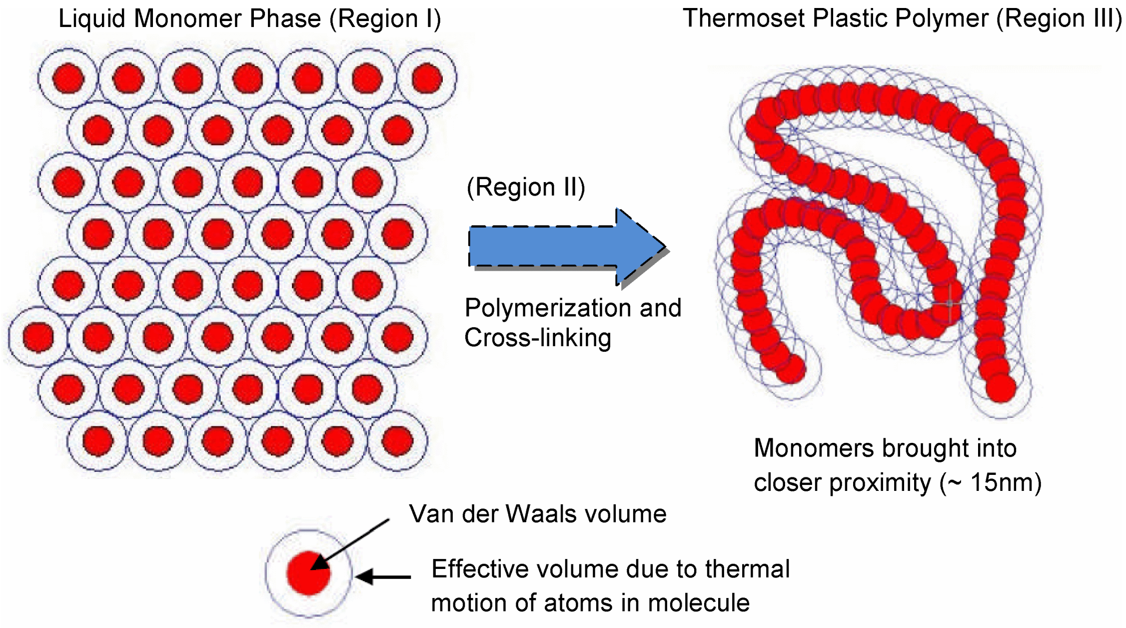
Resin System	Catalyst Agent	Gel-time [min] (at 25°C)	Chemical Shrinkage
Unsaturated Polyester (UP) Reichhold Norpol 420-100	0.5wt% NL 4NP Accelerator 2.0wt% Butanox M50 Initiator	10	7-10%[5, 6]
Unsaturated Polyester (UP) Reichhold Norpol 420-100	0.5wt% NL 4NP Accelerator 1.0wt% Butanox M50 Initiator	17	7-10%[5, 6]
Unsaturated Polyester (UP) Reichhold Norpol 420-100	0.25wt% NL 4NP Accelerator 1.0wt% Butanox M50 Initiator	28	7-10%[5, 6]
T-LAM 130-1 Slow Epoxy	40wt% T-LAM 130-1 Hardener	396	2-3%
Bisphenol A/F Epoxy	40wt% Bisphenol A/F Hardener	210	5-6%
Ampreg 21 Epoxy	33wt% Ampreg 21 Hardener	120	3.5-4.5%[17]
Standard Low Profile Additive (LPA)	-	-	-2%[6]

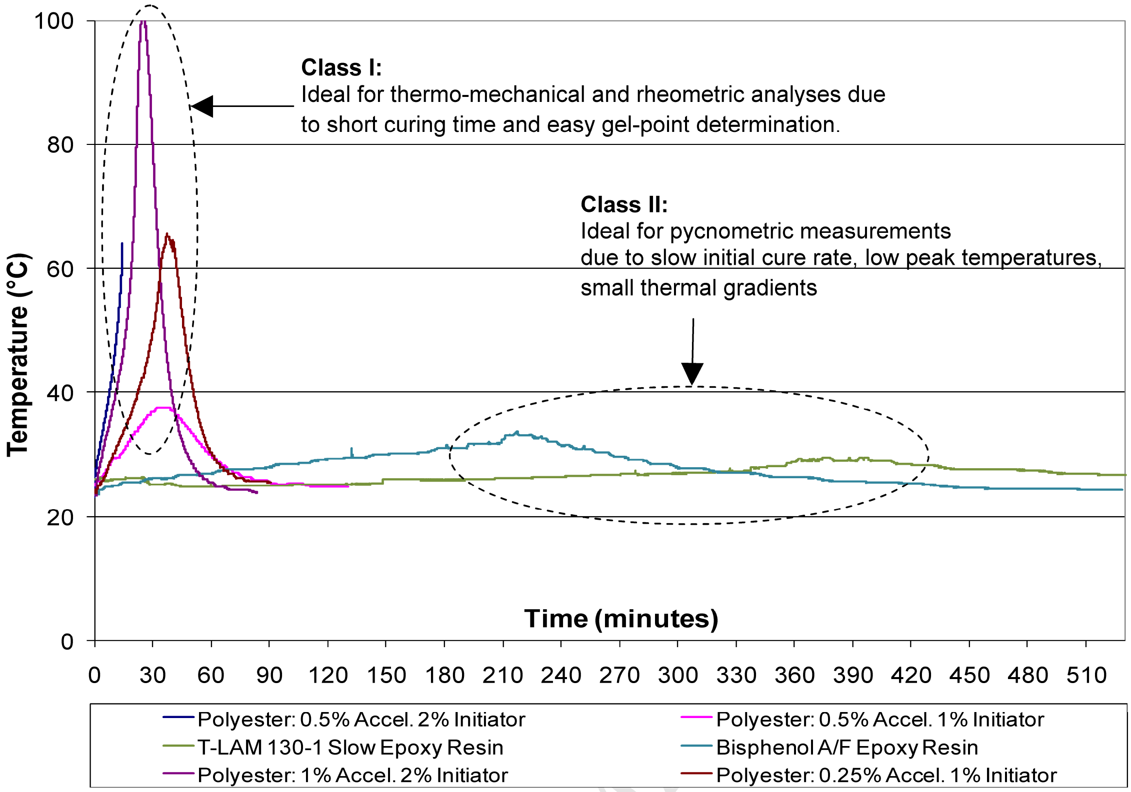
	Test 1	*Test 2*	*Test 3*	**Average**	**Standard Deviation**
Segments undertaken	*I,II*	*I,II*	*I,II,III*	***n/a***	
Time to Gelation [min]	29.2	27.5	30	**28.9**	**1.28**
G’ (or G’’) at Gelation [Pa]	12	17	15	**14.7**	**2.52**
Final gap size at Segment II [mm]	0.452	0.452	0.454	**0.453**	**0.001**
Final shrinkage at Segment II	9.30%	9.30%	8.92%	**9.17%**	**0.22%**
Final shrinkage at Segment III	-	-	9.10%	**9.10%**	**-**

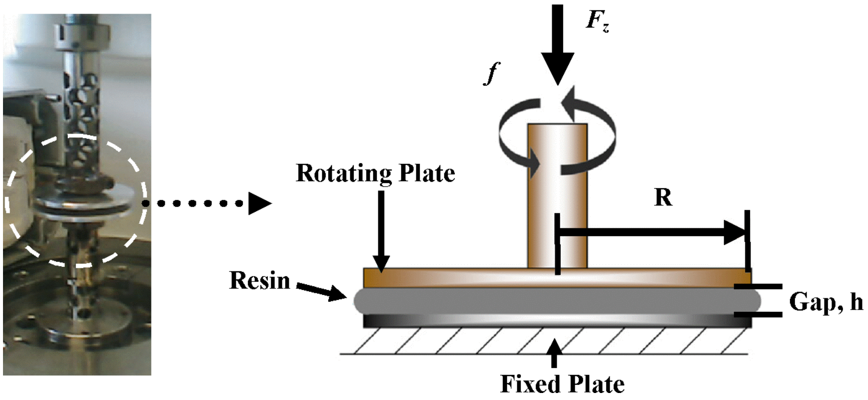
			% Shrinkage			
Resin System	**Cure Stage/Type**	**DoC**	Pycnometer	Rheometer	TMA	Expected
Unsaturated Polyester	Ambient Cure	85.0%	8.50	9.17	-----	7-10
	Post-Cure	99.0%	9.35	9.10	-----	
Epoxy	Ambient Cure	83.0%	4.10	3.67	-----	3.5-4.5
	Post-Cure	99.5%	4.10	3.67	-----	

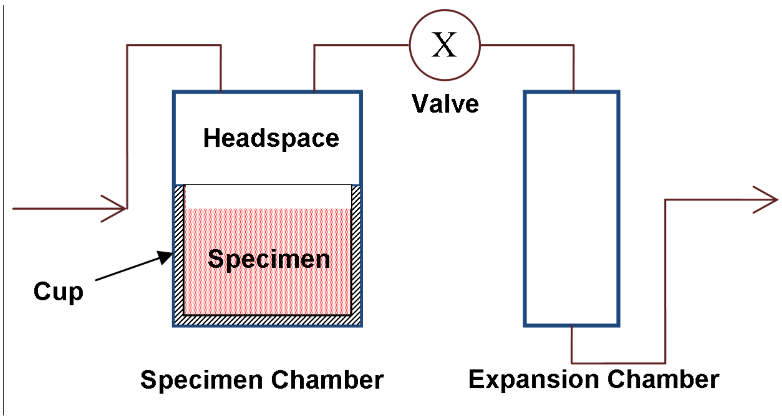

I
II
III
Specific Volume
Post-Gelation
Chemical Shrinkage
v_i
v_f
Time

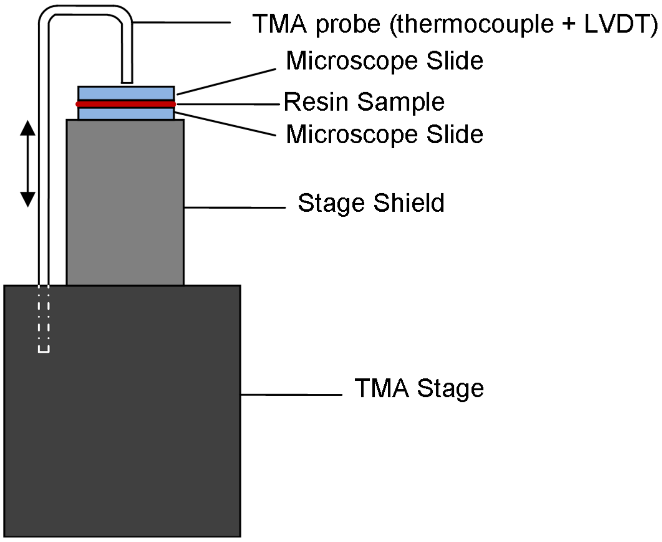

Liquid Monomer Phase (Region I)
Thermoset Plastic Polymer (Region III)
(Region II)
Polymerization and Cross-linking
Van der Waals volume
Effective volume due to thermal motion of atoms in molecule
Monomers brought into closer proximity (~ 15nm)

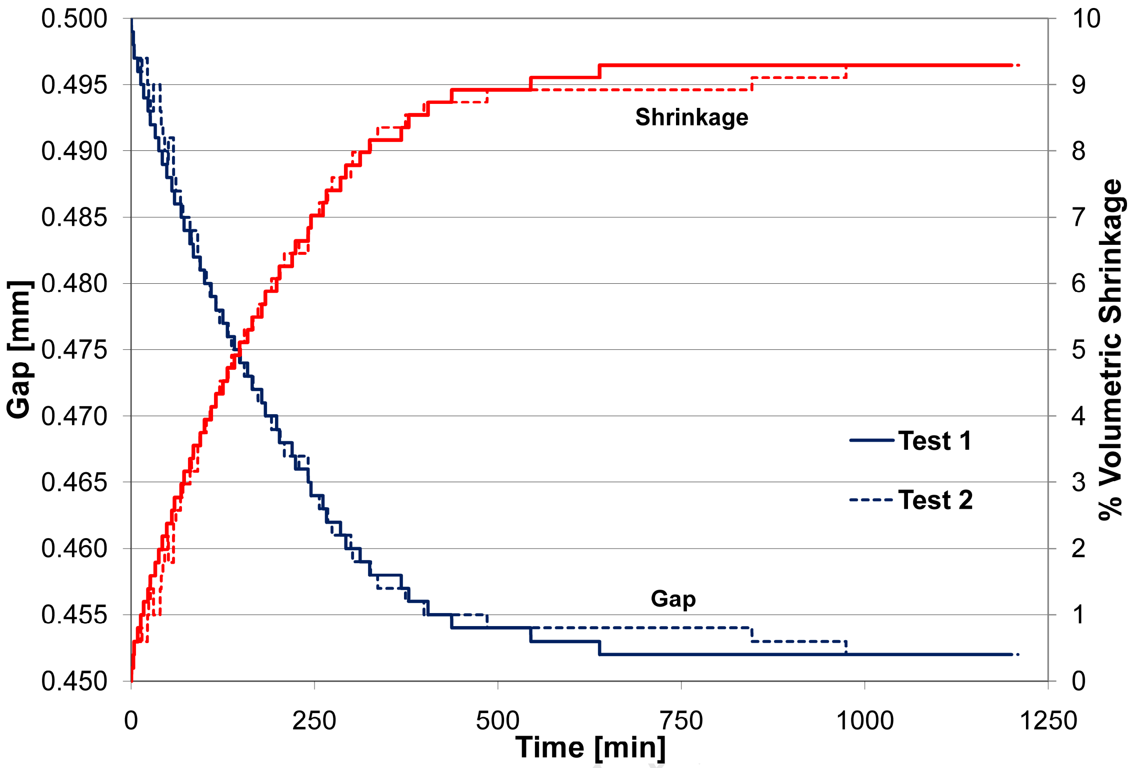

Liquid Monomer Phase (Region I)
Thermoset Plastic Polymer (Region III)
(Region II)
Polymerization and Cross-linking
Monomers brought into closer proximity (~ 15nm)
Van der Waals volume
Effective volume due to thermal motion of atoms in molecule

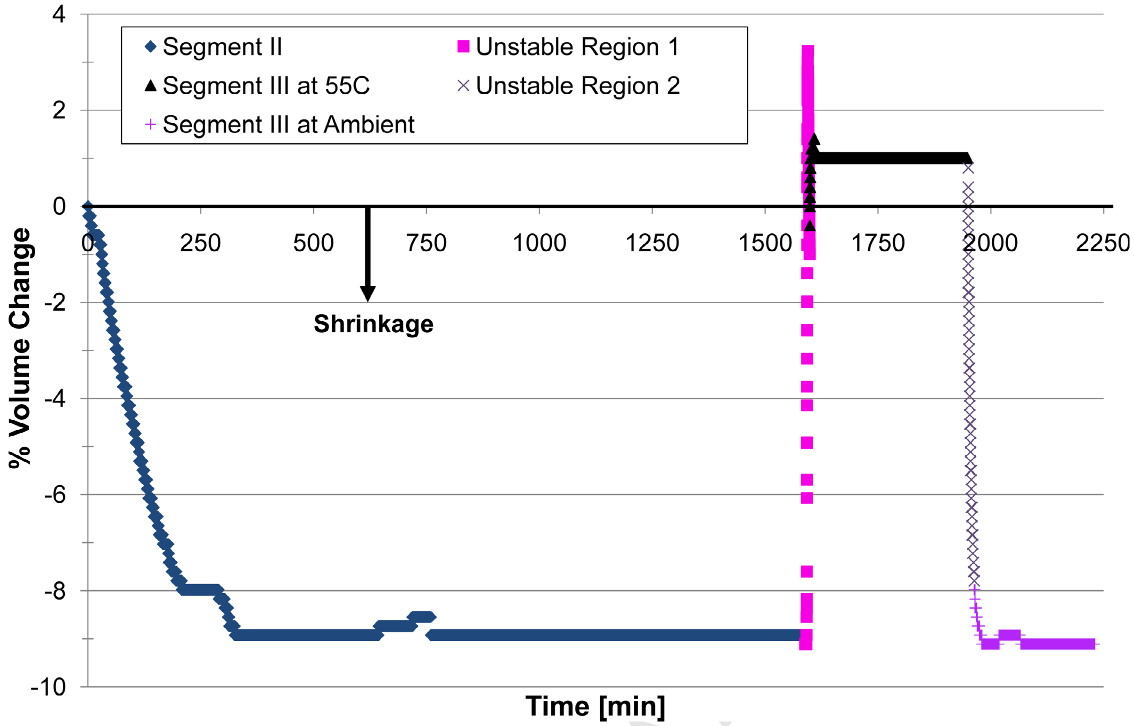

Temperature (°C)
100
80
60
40
20
0
Time (minutes)
0
30
60
90
120
150
180
210
240
270
300
330
360
390
420
450
480
510
Class I:
Ideal for thermo-mechanical and rheometric analyses due to short curing time and easy gel-point determination.
Class II:
Ideal for pycnometric measurements due to slow initial cure rate, low peak temperatures, small thermal gradients
Polyester: 0.5% Accel. 2% Initiator
Polyester: 0.5% Accel. 1% Initiator
T-LAM 130-1 Slow Epoxy Resin
Bisphenol A/F Epoxy Resin
Polyester: 1% Accel. 2% Initiator
Polyester: 0.25% Accel. 1% Initiator

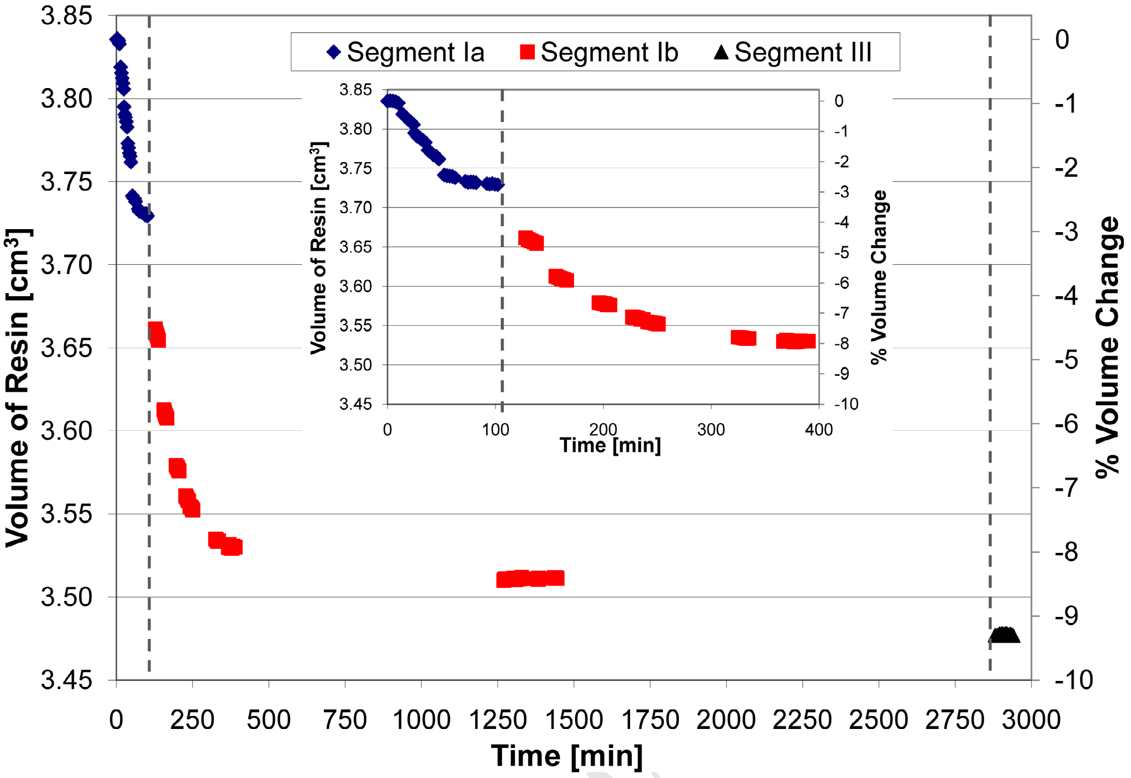

F_z
f
Rotating Plate
R
Resin
Gap, h
Fixed Plate

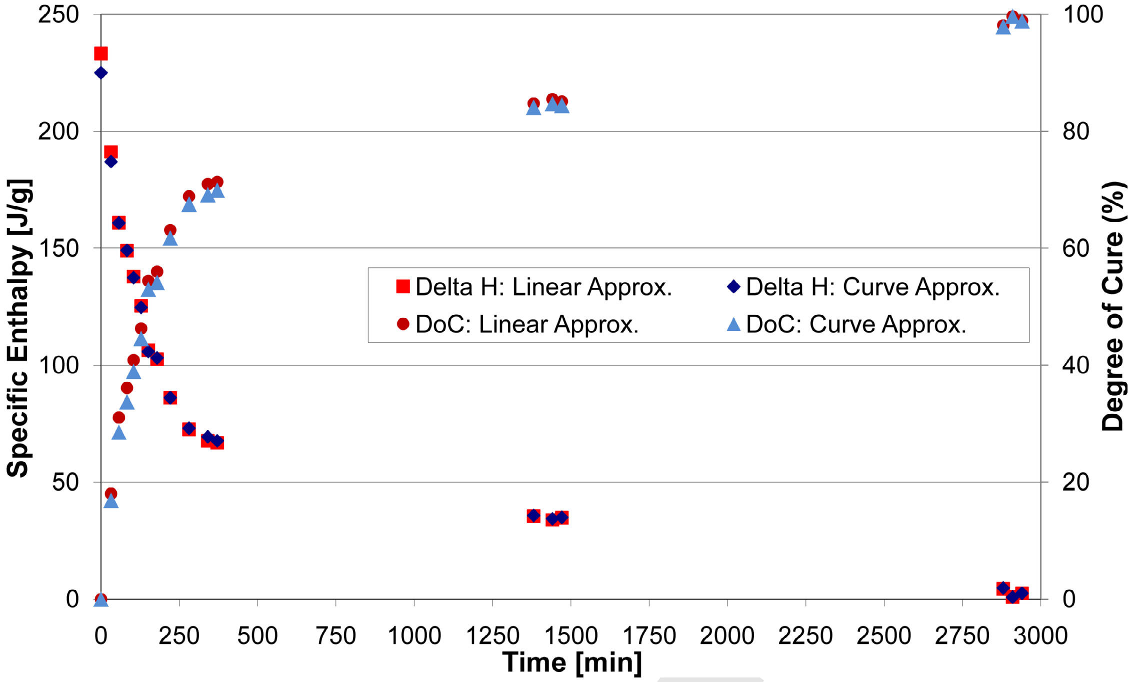

X
Valve
Headspace
Specimen
Cup
Specimen Chamber
Expansion Chamber

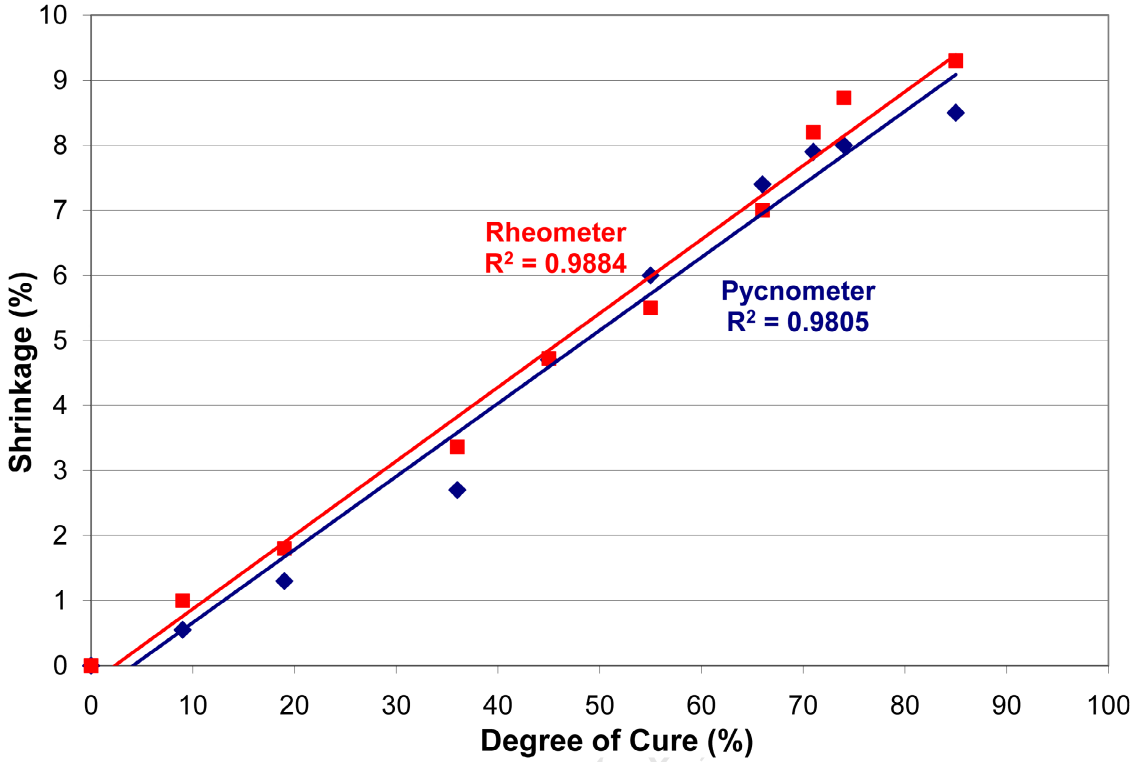

TMA probe (thermocouple + LVDT)
Microscope Slide
Resin Sample
Microscope Slide
Stage Shield
TMA Stage

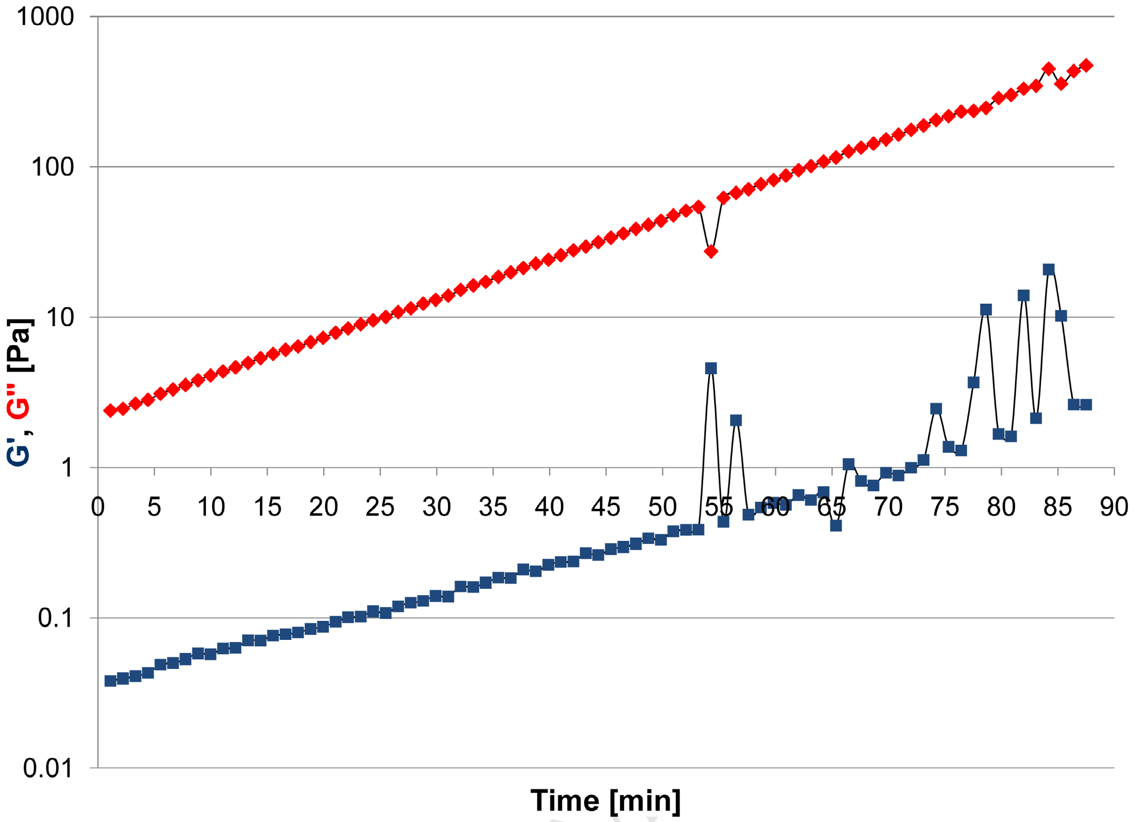

0.500
0.495
0.490
0.485
0.480
0.475
0.470
0.465
0.460
0.455
0.450
Gap [mm]
10
9
8
7
6
5
4
3
2
1
0
% Volumetric Shrinkage
0
250
500
750
1000
1250
Time [min]
Shrinkage
Gap
Test 1
Test 2

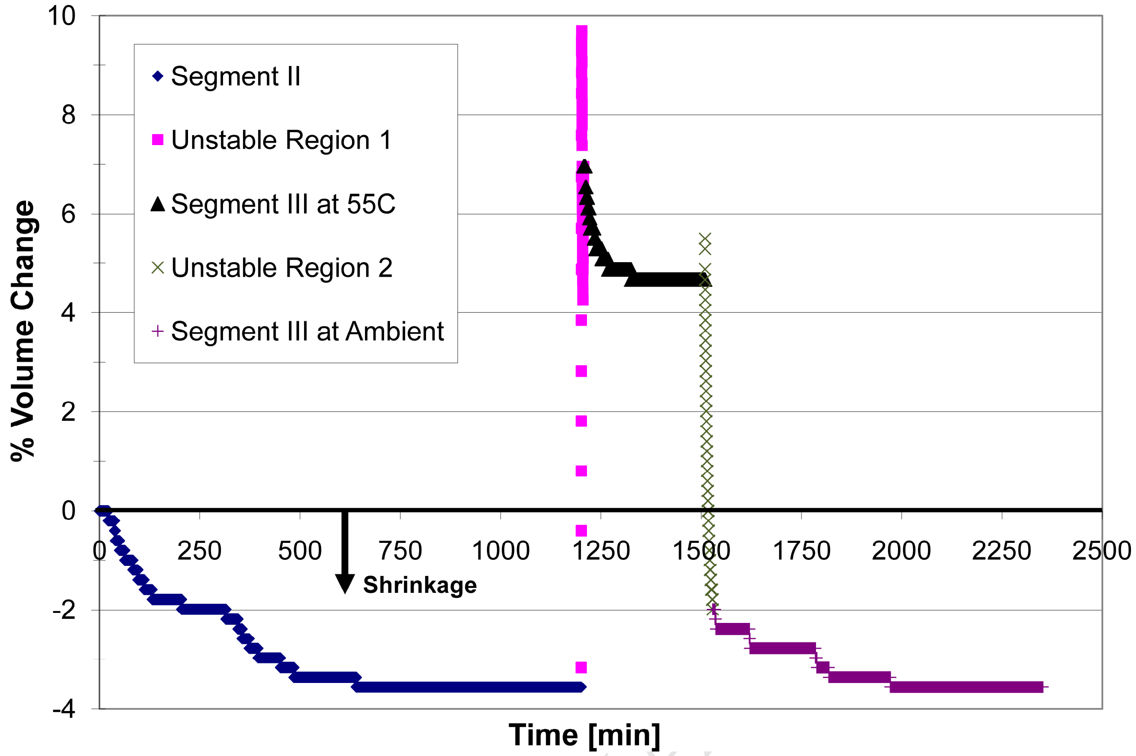

4
2
0
-2
-4
-6
-8
-10
% Volume Change
0
250
500
750
1000
1250
1500
1750
2000
2250
Time [min]
Shrinkage
◆ Segment II
▲ Segment III at 55C
+ Segment III at Ambient
■ Unstable Region 1
× Unstable Region 2

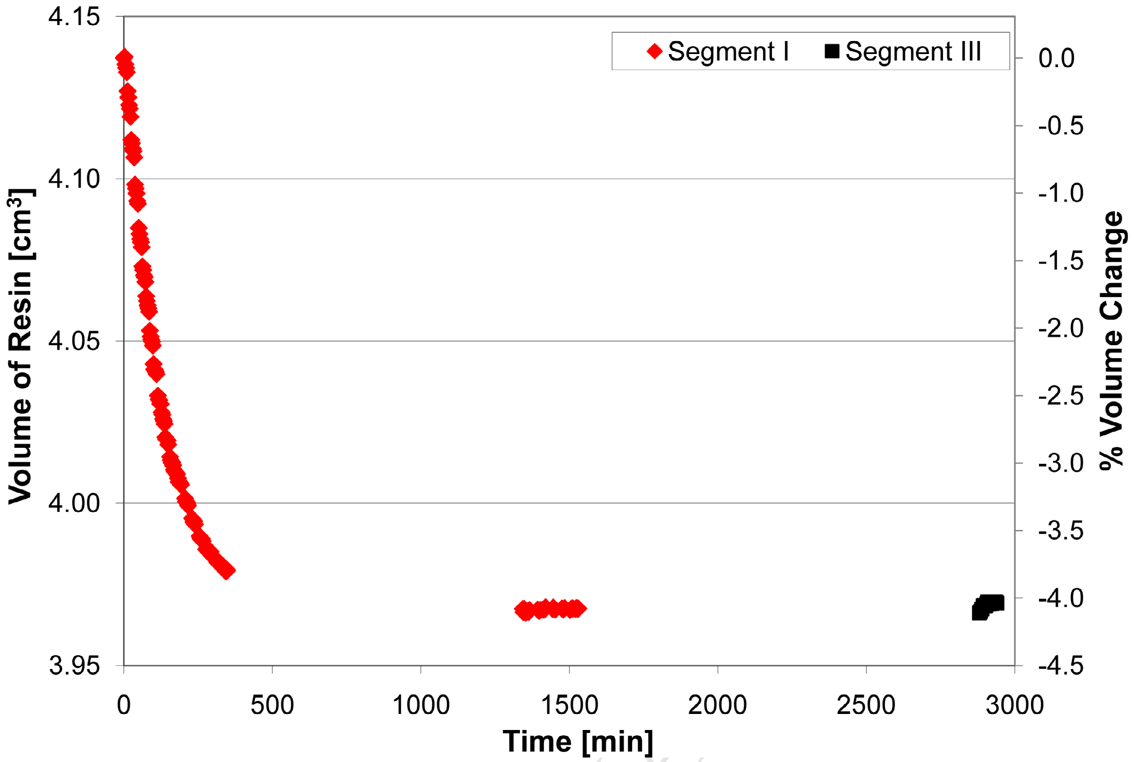

◆ Segment Ia
■ Segment Ib
▲ Segment III
Volume of Resin [cm^3]
3.85
3.80
3.75
3.70
3.65
3.60
3.55
3.50
3.45
% Volume Change
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
Time [min]
0
250
500
750
1000
1250
1500
1750
2000
2250
2500
2750
3000
0
100
200
300
400


Specific Enthalpy [J/g]
250
200
150
100
50
0
Degree of Cure (%)
100
80
60
40
20
0
0
250
500
750
1000
1250
1500
1750
2000
2250
2500
2750
3000
Time [min]
Delta H: Linear Approx.
Delta H: Curve Approx.
DoC: Linear Approx.
DoC: Curve Approx.


Shrinkage (%)
Degree of Cure (%)
Rheometer
R² = 0.9884
Pycnometer
R² = 0.9805
0
1
2
3
4
5
6
7
8
9
10
0
10
20
30
40
50
60
70
80
90
100


1000
100
10
1
0.1
0.01
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
G', G'' [Pa]
Time [min]


10
8
6
4
2
0
-2
-4
% Volume Change
0
250
500
750
1000
1250
1500
1750
2000
2250
2500
Time [min]
Shrinkage
◆ Segment II
■ Unstable Region 1
▲ Segment III at 55C
× Unstable Region 2
+ Segment III at Ambient


Segment I
Segment III
Volume of Resin [cm^3]
4.15
4.10
4.05
4.00
3.95
% Volume Change
0.0
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
-4.0
-4.5
Time [min]
0
500
1000
1500
2000
2500
3000