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Determination of Shrinkage and Modulus Development of Thermosetting Resins

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ABSTRACT: A new method for the determination of shrinkage and modulus development of thermoset resins is described. The method uses the change in the time of travel of longitudinal ultrasonic waves in a couplant to determine the change in height of a column of resin. This change in height is used to determine shrinkage. The method also uses the time of travel of ultrasonic waves through a column of resin to determine the modulus of the resin. The technique allows continuous monitoring of shrinkage and modulus as the material changes from the liquid state to the solid state. This method is used to determine the shrinkage and modulus development for a common epoxy resin.

KEY WORDS: thermoset resin, shrinkage development, modulus development, ultrasonic, spring-in.

INTRODUCTION

THE MANUFACTURING OF components made of advanced composite materials requires close control of the dimensions of the part. The curing of a component generally results in changes in volume and modulus. These variations can cause distortions in the configuration of a component. These variations can result in warping, errors in dimensions, residual stresses, and poor surface finish. Factors that affect the variations include properties of the tool materials, the geometry of the tool, the difference in coefficient of thermal expansion (CTE) between the tool and the composite material, and, to a large extent, the chemical shrinkage of the resin.

It is well known that resins shrink upon solidification. This shrinkage is due to both thermal expansion (contraction) and chemical shrinkage. For epoxies, the volumetric shrinkage can be as much as 6% [1–3]. For polyesters, this shrinkage can be even higher. Shrinkage of the resin plays a significant role in the residual stresses that develop within a part and the dimensional errors of the part. For the manufacture of high-quality aircraft composite components, for the control of surface finish in high-quality automotive composite parts, and for the tight dimensional control of the fitting of a crown on top of a

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Figures 1, 3–11 and 13–19 appear in color online: <http://jcm.sagepub.com>

tooth etc., the understanding and control of the shrinkage of the resin is important. The need to have dimensional control has been the subject of many recent investigations in the manufacture of advanced composite components [4,5].

Usually, information on the shrinkage of resin has been available only as a single number, i.e., the difference between the volume of a certain mass of the material in the liquid state and that in the solid state after curing is finished. This single number is the total shrinkage of the resin. However, it does not provide sufficient information for modeling of the behavior of the material and/or structure during the curing process. Information on the whole history of shrinkage would allow better models to be developed and thus permit better adjustment of the processing parameters to control the final part geometry.

The development of modulus resins during curing is important for the determination of residual stresses and resulting deformations in structures made of composite materials. Availability of the history of modulus development would significantly enhance the accuracy of models for residual stress and deformation.

For the measurement of shrinkage of resins there are a few techniques available. In the conventional method (for example, ASTM D6289) a certain mass of the resin is considered. The difference between the volume of this mass in liquid form and in solid form after curing is used to measure shrinkage. However, this single number does not provide information on the development of shrinkage during the solidification process. Snow and Armstead at the Naval Research Laboratory [6] used a simple capillary and bulb mercury dilatometer to make specific volume measurements in thermoset resins during the curing reaction as a function of temperature. They reported difficulties in monomer/prepolymer degassing, filling the dilatometer under vacuum, adhesive distortion of the curing resin in the dilatometer bulb and at the transition between the dilatometer bulb and the capillary.

A few designs for the monitoring of the history of shrinkage have been developed. Kinkelaar and Lee [7] developed a dilatometer for the measurement of shrinkage of low-shrink unsaturated polyester resins. This system places the resin to be examined inside a plastic pouch that in turn is placed in a cavity containing oil between two metal disks. The assembly is placed in a thermostat. A plunger in contact with the oil moves up and down depending on the expansion or contraction of the sample. Either a weight or pressure is used to keep the plunger in contact with the confined oil. The system was used to monitor the development of volumetric expansion or shrinkage of a few resin systems consisting of unsaturated polyesters and low profile additive. This design requires the venting of air from the plastic pouch and the confining oil. Russell et al. [8] used a PVT (Pressure Volume Temperature) apparatus for the measurement of volumetric shrinkage of epoxy resins. The two designs mentioned seem to have the ability to measure the shrinkage of thermoset resins during cure. However, the design and set up procedure is complex. It utilizes mercury to be in contact with the specimen. It also requires at least 10 MPa (1450 psi) for its operation. The PVT requires a good amount of space and can be quite noisy in operation. Recently Li et al. [9] developed a gravimetric method for the *in situ* measurement of chemical shrinkage of MY750 epoxy resin. In this Archimedes-principle method, a thin walled silicone bag is used to contain the resin sample. An aluminum plug is used to keep the resin sample inside the bag. A binding sleeve of polychloroprene rubber is used to seal the silicone rubber bag against a groove in the aluminum plug. The whole assembly of bag and plug is immersed inside a liquid silicone bath at a controlled temperature. The assembly of bag and plug is hung with a wire to an electronic scale. The reading on the scale is the net difference between the weight of the

assembly and the buoyancy force of the silicone liquid. The principle of operation is that the buoyancy force depends on the volume of the silicone rubber bag. If the resin inside the bag expands or contracts, the volume of the bag will change. This in turn affects the buoyancy force, which is recorded by the scale reading. This is an interesting technique, which is simple to implement. The results obtained show that the shrinkage seems to follow a similar trend as the curing of the resin.

In terms of measurement of modulus during the period of curing of the resin a few techniques have been attempted. One technique would be to perform mechanical tests on samples with different degrees of cure. However, one always has to wait until the resin sample is rigid enough for handling. Also the time required for handling the test specimens would introduce errors in the results. DMA tests can also be done. However, samples need to be rigid enough for handling and therefore only a portion close to the solid end of the spectrum can be examined. Ultrasonic techniques have been used to monitor the development of modulus. In 1991, Challis et al. [10] used ultrasonics to measure the modulus of an adhesive polymer layer as a function of frequency. They placed the adhesive layer between two glass blocks and coupled the ultrasonic transducers (UT's) to the surface of the glass blocks using compressed aluminium foil. In 1994, Thomas et al. [11] used a rheometer with piezoelectric ultrasonic oscillator to measure viscoelastic properties, including storage and loss shear moduli. In 1997, Alig et al. [12] used ultrasonic reflection techniques to measure the development of shear modulus of an adhesive layer. In 2003, Challis et al. [13] compared ultrasonic techniques to dielectric and nuclear magnetic resonance techniques to follow the network formation of an epoxy/amine system. Their work shows that ultrasonic measurement is a good technique to follow modulus development. The present authors have not found mention in the literature of a method that simultaneously measures both the shrinkage and the modulus of a resin in the process of curing.

A Polymer Shrinkage and Modulus (PSM) measurement system has been developed at the Concordia Centre for Composites [14]. This instrumentation is able to monitor the whole history of shrinkage of the resin from the liquid state to the solid state. It also provides information on the development of the modulus of the resin during the process. The shrinkage and modulus histories of a few resin systems commonly used for composites has been measured using the PSM instrument. This article presents the principle of operation of the PSM system and the results of the history of shrinkage and modulus for one epoxy resin.

PSM INSTRUMENTATION SYSTEM FOR THE MONITORING OF SHRINKAGE AND MODULUS

Figure 1 shows a schematic representation of the basic set up of the PSM system test cell. The procedure for running a test is as follows. Liquid resin sample is placed into the cup that has smooth surfaces inside and well-controlled dimensions. Liquid couplant is placed on top of the liquid resin sample. It is important that the liquid couplant be less dense than the liquid resin and also chemically inert and immiscible with respect to the resin system.

The UT is held fixed in the cup cover so that it is partially immersed in the liquid couplant. The cup must be set up so that it is in a horizontal position, i.e., the cup bottom must be parallel to the liquid interface between the couplant and the resin. The test cell can be placed inside a thermostat as required. The UT is connected to a pulser/receiver card in a PCI slot of a personal computer. The same card is used to monitor couplant temperature

with a thermistor. The system acquires, treats, and stores the ultrasonic signals and the temperature at used-specified time intervals. Figure 2 shows a schematic of the setup.

The liquid resin must be carefully poured into the center of the cup bottom so that it only touches the cup walls as a result of slow, gravity filling. After the liquid couplant is gently flowed on to the top of the resin, the test can begin.

The principle of operation is now presented. The UT produces a longitudinal sound wave that travels into the couplant. When the wave arrives at the interface between the couplant and the resin, some of it is transmitted into the resin and some is reflected back through the couplant to the UT where it is transduced into an electrical pulse. We call this pulse 'first couplant/resin interface reflection' (see Figure 3 for these features). The part that is transmitted through the resin will itself be reflected at the resin/cup interface and eventually strike the UT, producing a second electrical pulse called 'first resin/cup interface reflection'. The ultrasonic wave will reflect and transmit at these interfaces until its

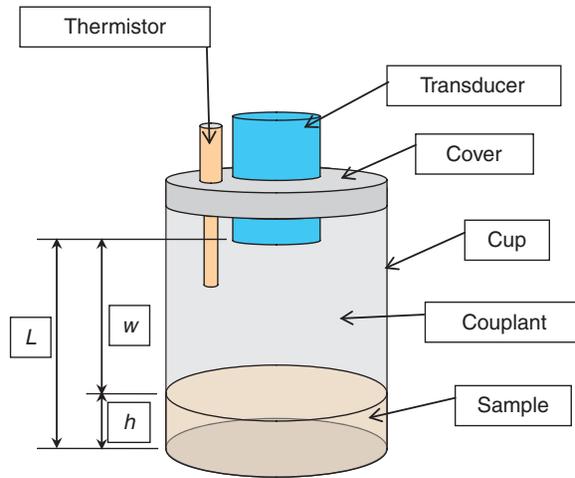


Figure 1. Schematic of PSM test cell.

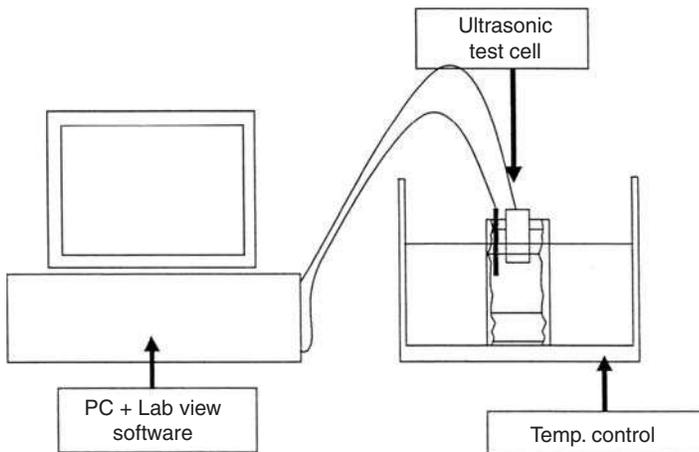


Figure 2. Schematic of the PSM instrumentation setup.

pressure amplitude becomes too small to be recorded. In any case, we only need the two reflections mentioned above, plus the ‘second couplant/resin interface reflection’, the latter being the result of a second round trip in the couplant only. These three pulses are part of the information used to measure shrinkage and modulus as explained below.

Determination of the Shrinkage Coefficient Using the Part of the Beam that is Reflected from the Couplant/Resin Interface

Referring to Figure 1, let L represent the distance between the UT and the inside bottom of the cup. Let h represent the height of the resin sample, and w represent the distance between the UT and the couplant/resin interface. We have:

$$w = L - h. \tag{1}$$

Let v_c represent the speed of sound in the couplant. The time, t_c , required for the wave to make one round trip (i.e., $2w$) between the UT and the couplant/resin interface is:

$$t_c = 2 \frac{w}{v_c} = 2 \frac{L - h}{v_c}. \tag{2}$$

which can be rewritten as

$$h = L - \frac{t_c v_c}{2}. \tag{3}$$

Letting d represent the inside diameter of the cup, the volume of the resin is expressed as

$$V_r = \frac{\pi d^2}{4} \left(L - \frac{t_c v_c}{2} \right). \tag{4}$$

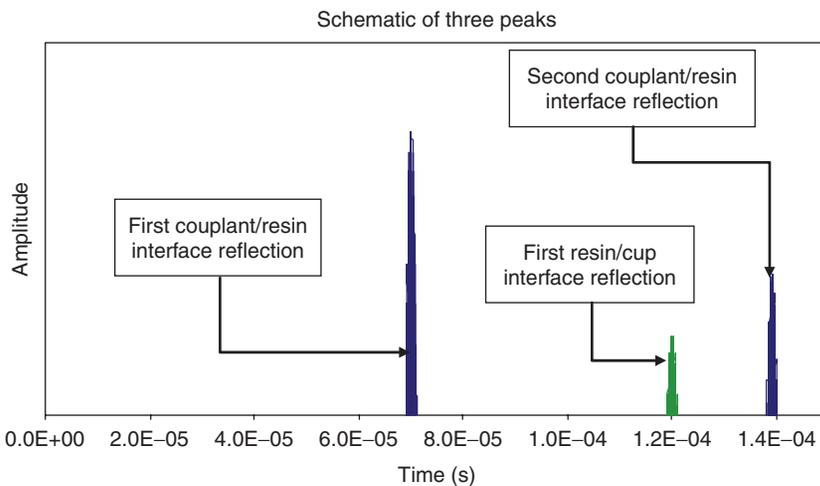


Figure 3. Schematic of three pulses from the ultrasonic readout.

Figure 3 shows a schematic example of a typical PC screen display. During the test, the software modules extract the time difference between the first pulse and the third pulse (i.e., the time of flight (TOF) for a round trip in the couplant, t_c) and the volume of the resin is calculated using Equation (4). To account for the effect due to temperature variation, the speed of propagation of the ultrasonic wave in the couplant, v_c , must be known as a function of temperature. If this data is not already available, the PSM system can be used to measure v_c as a function of temperature (as discussed below.) Also the diameter, d , of the cup is adjusted for thermal expansion effects using the following equation:

$$d = d_o(1 + \alpha\Delta T), \quad (5)$$

where d_o is the initial diameter of the container, ΔT is the change in temperature, and α is the CTE of the cup material (assumed constant). The coefficient of shrinkage, S , is defined as:

$$S = \frac{V_o - V_r}{V_o}, \quad (6)$$

where V_r is the instantaneous resin volume calculated using Equation (4) and V_o is the initial volume of the resin.

During the course of a test, if the resin volume changes the couplant/resin interface will move and the time of travel of the ultrasonic wave to that interface will change. Thus, by monitoring the variation of t_c as cure progresses, and adjusting the diameter d for the temperature changes, the volume of the resin can be continuously monitored using Equation (4). Equation (6) is then used to determine the shrinkage of the resin as the cure progresses. It should be noted that, in general, the shrinkage is the algebraic sum of both thermal expansion and chemical shrinkage. After the resin returns to the original temperature, only chemical shrinkage remains.

Determination of Change in Modulus Using Information from Part of the Ultrasound Wave that Travels through the Resin

The part of the ultrasonic wave that is transmitted through the couplant/resin interface will reflect from the resin/cup interface and be detected by the UT. This reflection is represented by the middle pulse in the schematic shown in Figure 3 above. The time difference between the first pulse and the middle pulse represents the TOF of the ultrasonic wave for one round trip through the resin. Letting this time be t_r , we have:

$$v_r = \frac{2h}{t_r}, \quad (7)$$

where h is the resin height and v_r is the speed of propagation of the ultrasonic wave in the resin. The height of the resin is available using Equation (3). The speed of sound is related to modulus and density as follows:

$$v_r = \sqrt{\frac{M_r}{\rho_r}}, \quad (8)$$

where M_r is the effective modulus [15, p. 262] of the resin and ρ_r is the density of the resin. The resin density is given by:

$$\rho_r = \frac{m_r}{V_r}, \quad (9)$$

where m_r , the mass of the resin is assumed to be constant, and V_r is the volume of the resin, calculated using Equation (4). Combining Equations (8) and (9) gives:

$$M_r = \frac{m_r}{V_r} v_r^2. \quad (10)$$

During a test, the volume V_r at any particular time is calculated using Equation (4). The speed of propagation in the resin is calculated using Equation (7) in which the height h is obtained using Equation (3) and the time t_r is the time interval between the first pulse and middle pulse as represented in Figure 3.

Note that M_r is the, so-called, effective modulus of the resin. M_r is equal to $(K + 4G/3)$ where K is the bulk modulus and G is the shear modulus [13,15]; note that, in general, these moduli may be complex quantities. While the resin is in the liquid state, G is negligible and the modulus reported equals the bulk modulus K . As the resin becomes solid, G is no longer negligible and the modulus reported equals $(K + 4G/3)$. The effect of bulk and shear moduli cannot be distinguished in the reported data.

In summary, by monitoring changes in the time interval between the left pulse and middle pulse, t_r , and the time interval between the left pulse and right pulse, t_c , as shown in Figure 3, we can monitor the development of resin modulus and shrinkage, respectively.

VERIFICATION AND CALIBRATION OF THE PSM SYSTEM

To verify the performance of the PSM system the behavior of a substance with accurately known physical properties is needed. Because the authors are not aware of a resin with such generally accepted characteristics, water was chosen as reference material. Density of water as a function of temperature can be obtained from several sources (e.g., Reference [16]). The speed of sound in water as a function of temperature is taken from [17]. The data gathered in the tests are mass, temperature, and TOF.

First we verify the PSM system's accuracy in measuring TOF. Figure 4 shows plots of measured speed of sound in water as a function of temperature. The sketch in Figure 4 shows the setup used. A 20 mm gage block was used as the reference length, along with its CTE of $9.3 \mu\text{m/m}$, and the TOF was measured between the reflection from the top of the block and the bottom of the cup. The speed of sound was then calculated as the temperature varied between 20° and 90°C . The error is reported in percent and varies from $+0.1\%$ and -0.2% . This error can be due to inaccuracies in TOF measurement, temperature measurement, and/or length measurement. The 20 mm length of the gage block has an uncertainty of $\pm 0.1 \mu\text{m}$ and its CTE has an uncertainty of $0.5 \mu\text{m/m}$. These uncertainties are not significant for our current purpose.

The data shown in Figure 4 can also be reported in terms of measured and reference TOF. Figure 5 shows the error in TOF with a line fit through the error data. This error may be due to error in the TOF measurement itself and/or error in the temperature measurement.

The dependence of the speed of sound on temperature is least in the temperature interval from 70° to 80°C. Figure 5 shows that the error in this interval is about 10 ns. Since this is the resolution of our measurement system, we consider that whatever error exists, it is due only to the error in temperature measurement. When the temperature readings are

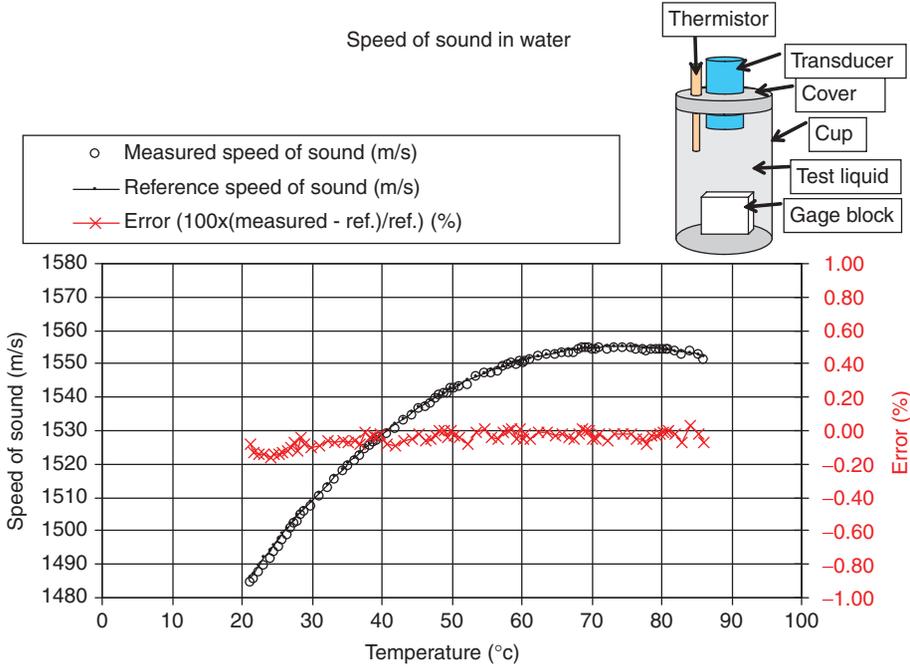


Figure 4. PSM verification using speed of sound in water.

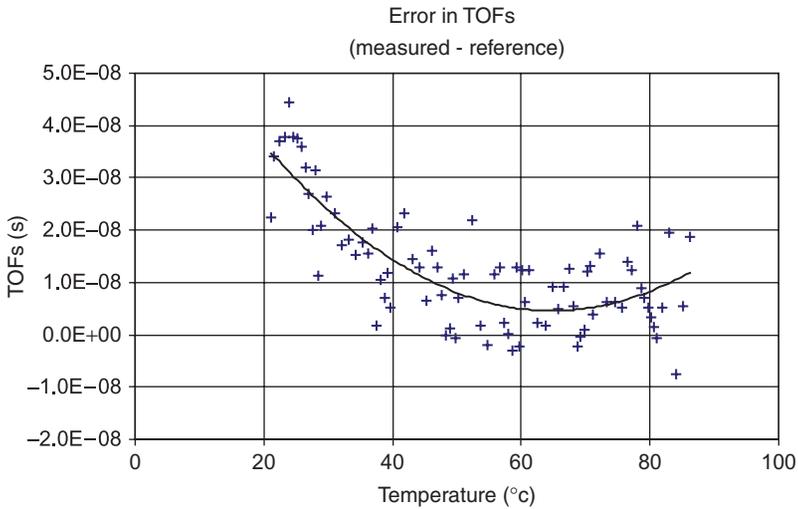


Figure 5. Error in TOF using speed of sound in water.

uniformly reduced by -0.5° , the errors in speed of sound measurements are reduced as shown in Figure 6, with an error range of -0.09% to $+0.05\%$.

Having performed the verification discussed above we now measure the change in water density as a function of temperature and will use the results to calibrate the whole PSM instrument. Thus, we use water as the sample, and we chose n-decane as couplant.

However, we need to know the speed of sound in n-decane (i.e., v_c) before we can carry out a standard test. This is conveniently done by repeating the test setup mentioned above to verify the speed of sound in water (Figure 4). The results, corrected for temperature by -0.5° , are shown in Figure 7, where a linear fit to the data is shown as well as experimental data points from [18] and [19], DATA SET 1 and DATA SET 2, respectively. We use the linear fit in a standard test with water as the calibration sample.

In our experiments ~ 28 g of water were used as the sample. The change in density of the water as the temperature changed from $\sim 21^\circ\text{C}$ to about 90°C was measured using the PSM instrument. Figure 8 shows results of density calculations, before the application of a calibration factor, along with reference values. Over this temperature range, the density of water decreases from $\sim 1000\text{ kg/m}^3$ to $\sim 965\text{ kg/m}^3$. The difference between the measured values and reference values are from -0.6% to -0.9% .

After application of a calibration factor of 1.0075, while the error range changes slightly (-0.15% to 0.19%), the absolute values are more accurate. Note that the calibration factor is used to compensate for uncertainties in mass, diameter, and CTE of the cup material.

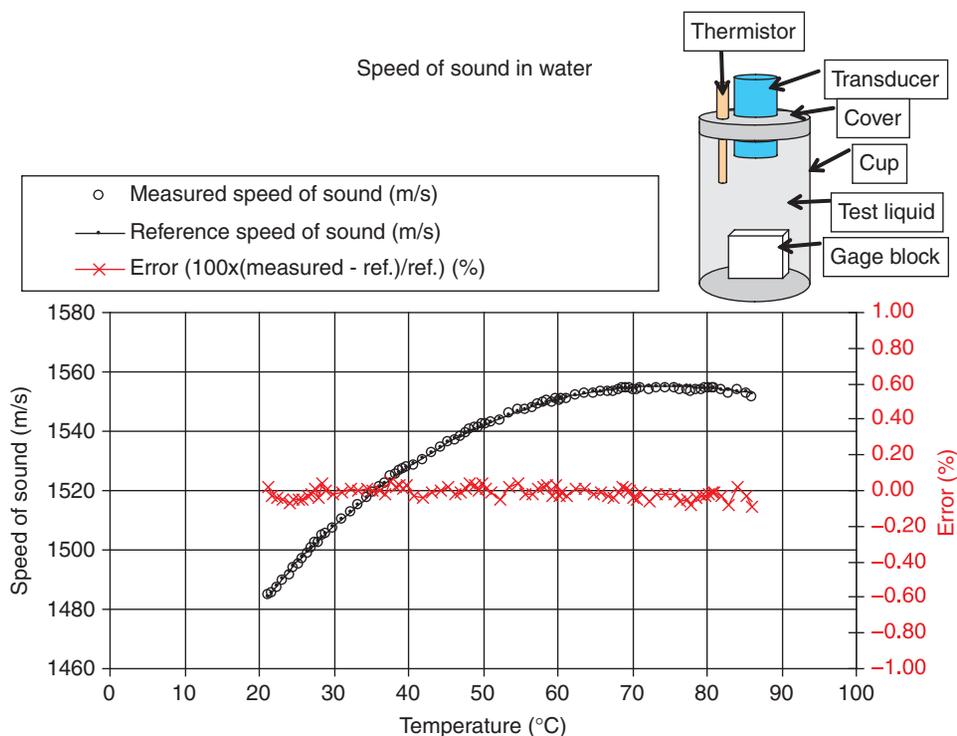


Figure 6. Speed of sound in water after temperature correction of -0.5°C .

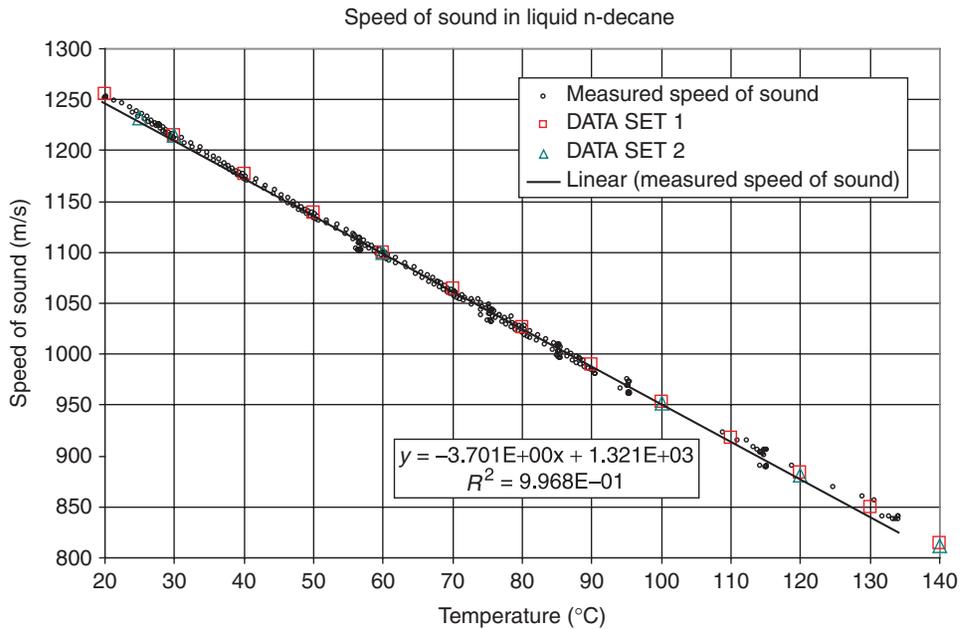


Figure 7. Measured speed of sound in n-decane.

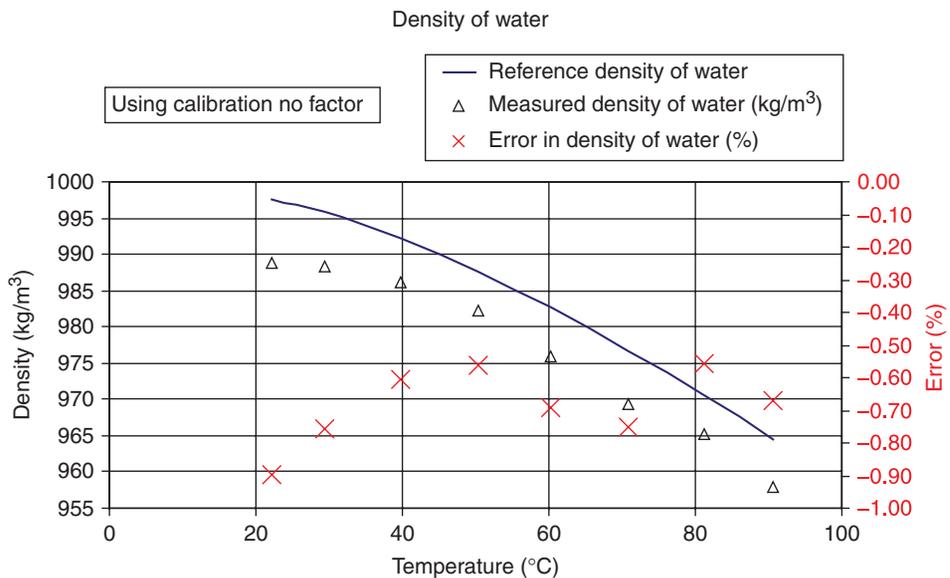


Figure 8. Water density measurements before application of a calibration factor.

The density measurements can be used to calculate shrinkage by assuming that the mass of the water remains constant. The measured shrinkage of water is compared to the reference values in Figure 10. The measured modulus of water is compared to the reference value in Figure 11. Since water has negligible shear stiffness, this is the bulk modulus, K .

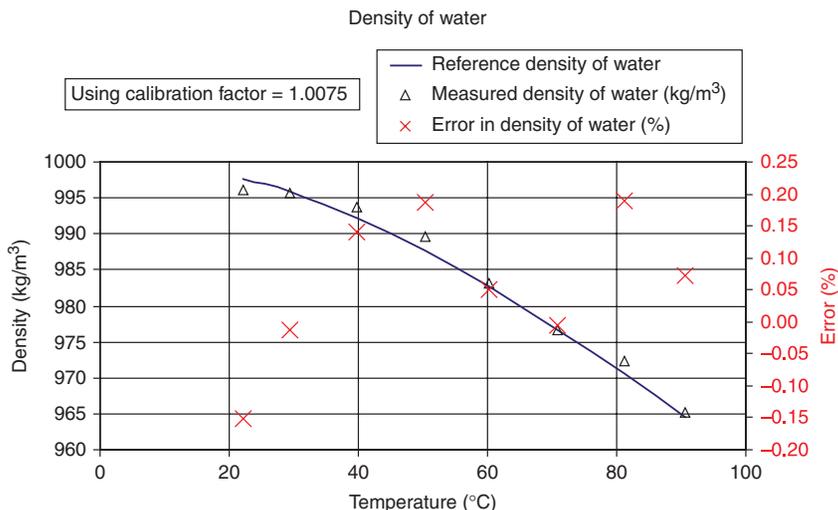


Figure 9. Water density measurements after application of a calibration factor.

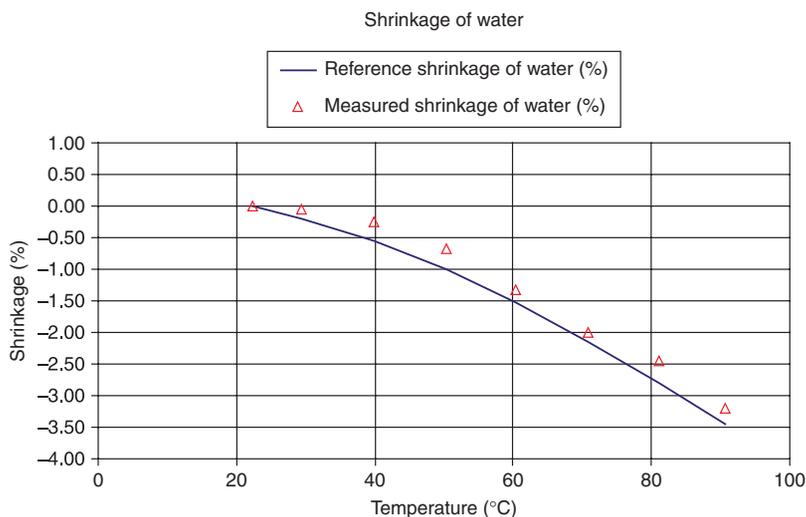


Figure 10. Water shrinkage.

USE OF THE PSM FOR RESINS

Limitations of the Method

The technique using the PSM instrumentation presented above can provide values of shrinkage and modulus of a sample on a (practically) continuous basis. To produce adequate results the user should note the following points

1. Resin sticking to or separating from the wall of the container:

It is important to ensure that the resin does not stick to the walls of the cup nor separate from its walls. Sticking of the resin to the walls inhibits free shrinkage. This can be

prevented by making sure that the container is made of material with very smooth inner surfaces. Currently, stainless steel and aluminum cups are used. Use of mold release agent inside the cup may be found useful. On the other hand, if the resin separates from the walls then the use of the inside diameter of the cup to calculate the volume of the resin will produce errors. A simple test will help to determine whether the cured resin separates from the walls. Colored alcohol can be poured on top of the cured resin, allowed to stay for 1 min and then wiped off. When the cured resin disk is taken out of the cup, the walls can be examined to see if the colored alcohol has seeped between the resin and the cup walls. For the tests carried out so far, no separation from the wall was observed. If the resin sticks to the wall of the container, this can give rise to a concave or convex upper surface of the resin block. This is discussed below.

2. *The top surface of the resin column may not be flat due to sticking to the wall of the container:*

In order to determine whether the top surface of the resin is flat, the thickness of cured resin blocks was crudely measured using a vernier caliper. Figure 12 shows the diametral line where thickness measurements of the block of resin were taken.

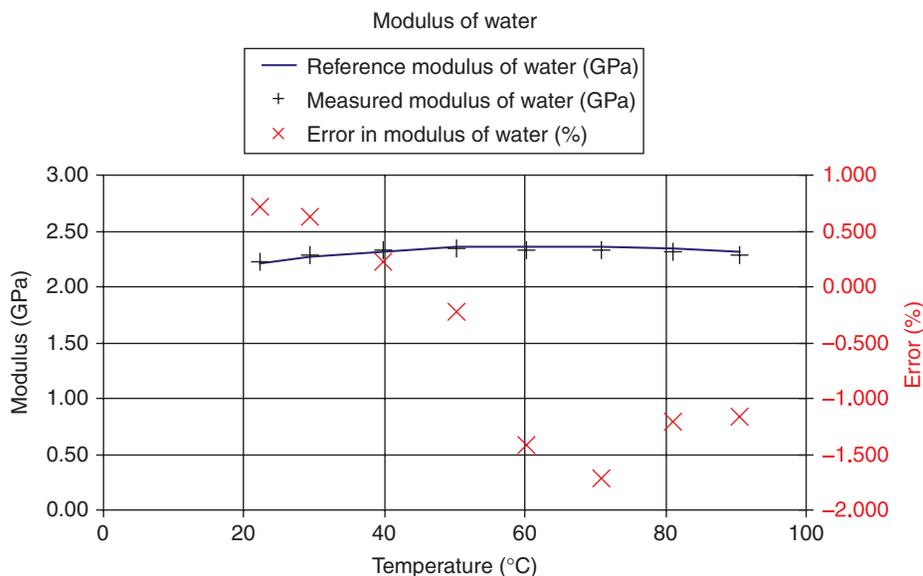


Figure 11. Water (bulk) modulus.

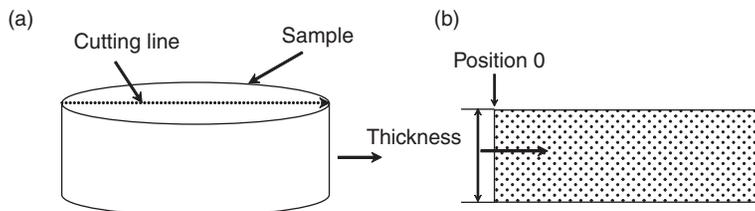


Figure 12. Schematic showing line for thickness measurement on a block of cured resin.

The thickness measurements for two resin systems (Epon 828/Epicure 3046, and Dow 324/Ancamine 2167) are shown in Figure 13. In this figure, the thickness of the cured blocks of resin shows fluctuations about a mean value, but there is no clear trend of curvature of the surface. This suggests that the surface of the resin is not distorted due to sticking to the PSM cup walls.

A surface profilometer with a resolution of 1 nanometer was also used to measure the surface roughness of the top surface of the cured resin blocks. Figure 14 shows the roughness of the top surfaces of the same two resin blocks used for Figure 13. Again there are fluctuations along the diametral line of the surface of the resin blocks, but there is no clear trend of curvature. The fluctuations depend on the type of resin system and its magnitudes can vary from $\pm 2 \mu\text{m}$ to $\pm 20 \mu\text{m}$.

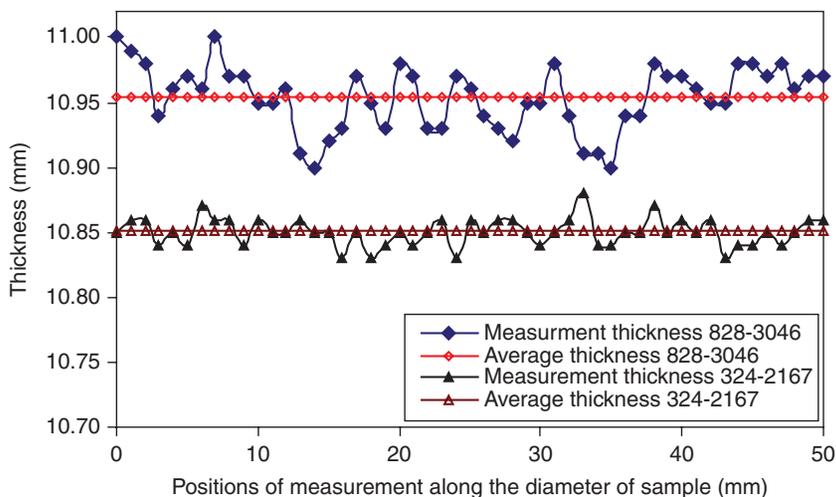


Figure 13. Surface profiles of top surface of resin blocks of two resin systems.

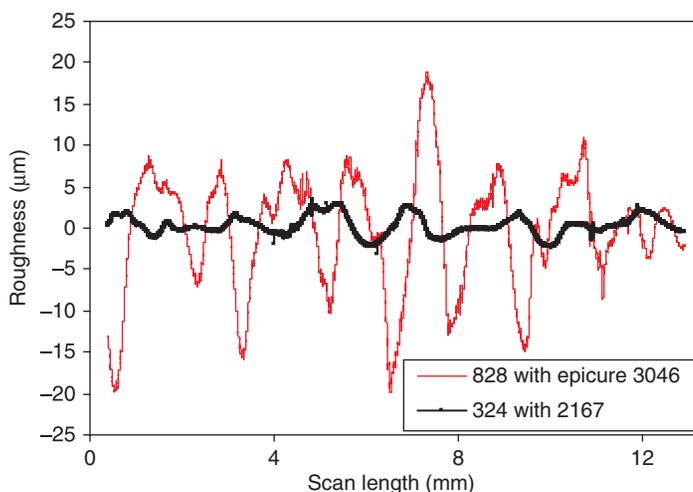


Figure 14. Surface roughness of the top surface of two cured resin blocks.

Evaporation of the Couplant During the Test

During the test some couplant will evaporate; the amount of couplant lost will depend on the boiling point of the couplant, the cure temperatures used, and the test duration. It is important that sufficient couplant is added at the beginning of a test so that the bottom surface of the UT is always immersed inside the couplant. The configuration of the PSM test cell permits this condition to be fulfilled.

Mixing between the Couplant and the Resin Materials

It is important that the couplant be both chemically inert and immiscible with respect to the resin. Different couplants were considered to find a suitable one. For the resin system and temperatures used here, decane was used as a couplant. Also it is important to check the appearance of the surface of the cured resin to see if there is any change in appearance due to diffusion of couplant into the resin. In the tests reported in this paper, no change in appearance on the surface of the cured resin was observed.

Amount of Resin Used

The amount of resin used may have an effect on the coefficient of shrinkage. This is due to the exothermic reaction of the resin during the process of cure. A larger block of resin will create more exothermic heat. As a result, there can be a significant temperature gradient from the center to the edge of the block of resin. In order to have results that may be comparable, the amount of resin should be similar in all tests. In the experiments reported here, resin of 10 mm deep in a cup of 46 mm diameter was used.

Time of Test

The delay time from the time of first mixing to the time when the first data is recorded may have an effect on the amount of shrinkage measured. This is because the reaction may start right after mixing and some shrinkage may already have taken place before the first reading is taken. As mentioned above with respect to the amount of resin used, it may be appropriate to use a fixed time delay for comparison purposes. In the tests reported here, a time period of about 20 min was required for removing the bubbles in the resin and another 10 min were used for test set up.

Determining the Times of Travel

The determination of TOF of the ultrasonic wave depends on the ability to set up the PSM so that the three required pulses shown in Figure 3 are 'visible' throughout a test. In Figure 3, which is only a schematic representation, there are three easily distinguished pulses, but this is not always the case. The middle peak is often the lowest peak because it represents travel through the highly attenuative resin, while the peak on the right-hand side is smaller than the left peak because it is the second reflection from the couplant/resin

interface and its path of travel in the couplant is twice as long. It is necessary that a UT be selected with enough power to avoid the loss of the middle pulse that is needed to measure t_r and calculate modulus. The instrument electronics must have a large dynamic range and a good signal/noise ratio to ensure faithful capture of the three pulses.

SHRINKAGE AND MODULUS DEVELOPMENT OF AN EPOXY RESIN

SHELL EPON 828 Epoxy and EPICURE 3046 Hardener

Shell Epon 828 with Epicure 3046 hardener is a common epoxy resin system. For these tests, two different transducers (from Sigma Transducers Inc.) with different powers were used. Transducer 1 has a diameter of 10 mm and a mean frequency of 5 MHz. Transducer 2 has a diameter of 19 mm and a mean frequency of 5 MHz. The results using transducer 1 are shown in Figure 15 and the results using transducer 2 are shown in Figure 16.

A 20-g mixture of epoxy and hardener was placed in an aluminum cup in room temperature air. Figure 15 show the temperature variation, shrinkage curves, and modulus

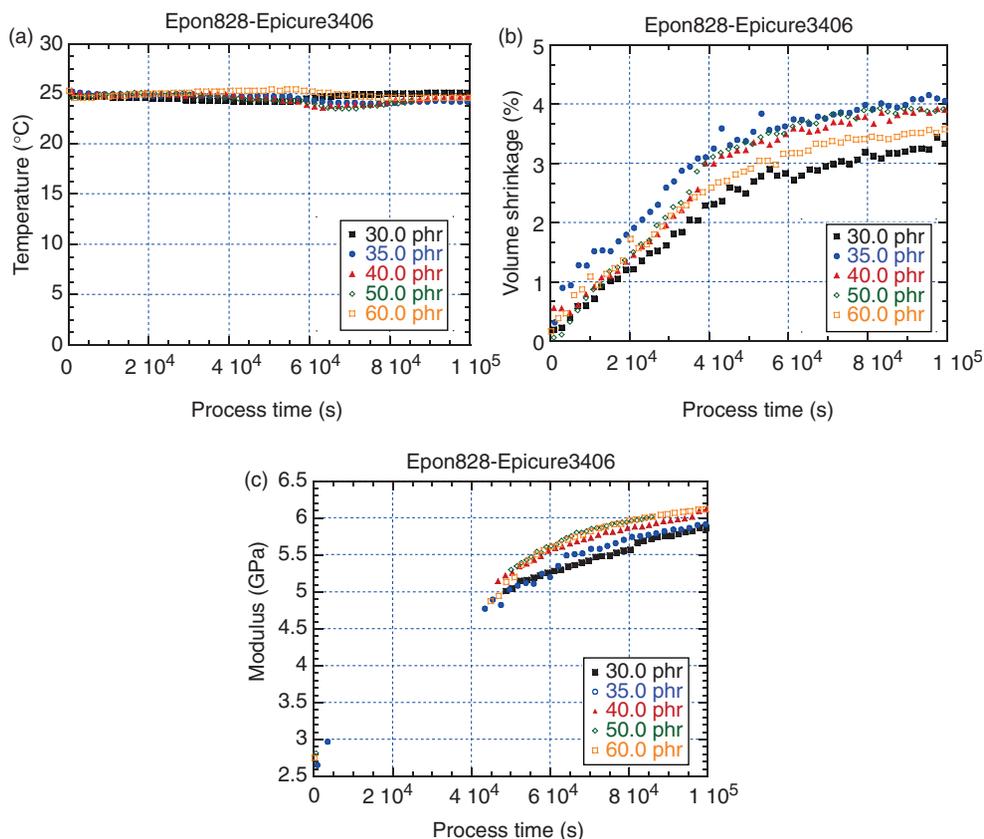


Figure 15. (a) Temperature variation during tests on samples with different amounts of hardener (Epon 828/Epicure 3046) (transducer 1); (b) Shrinkage of samples with different amounts of hardener (Epon 828/Epicure 3046) (transducer 1); (c) Modulus variation in samples with different amounts of hardener (Epon 828/Epicure 3046) (transducer 1).

curves for samples of Epon 828 resin with different amounts of hardener (Epicure 3046) tested with transducer 1. Figure 15(a) shows that the temperature does not vary much from one sample to another over the course of the test.

Figure 15(b) shows the shrinkage curves for samples with different amounts of hardener. The stoichiometric amount is close to 50 phr. The shapes of the shrinkage curves are similar, but samples with 35 phr, 40 phr, and 50 phr of hardener, shrink more than those with 30 phr and 60 phr of hardener. This can be explained by the fact that for samples with 30 phr of hardener (less than the stoichiometric ratio) there are less primary and secondary amines for curing. As such there are free epoxy ends still remaining in system. Similarly when the amount of hardener is up to 60 phr (more than stoichiometric ratio), there are some amines left after curing at room temperature. The free amines or epoxy ends are not well packed and the structure is not tight (shrinks less).

Figure 15(c) shows the development of the modulus of Epon828-Epicure 3046. Beginning at a modulus of about 2.7 GPa, the modulus curves show a discontinuity at

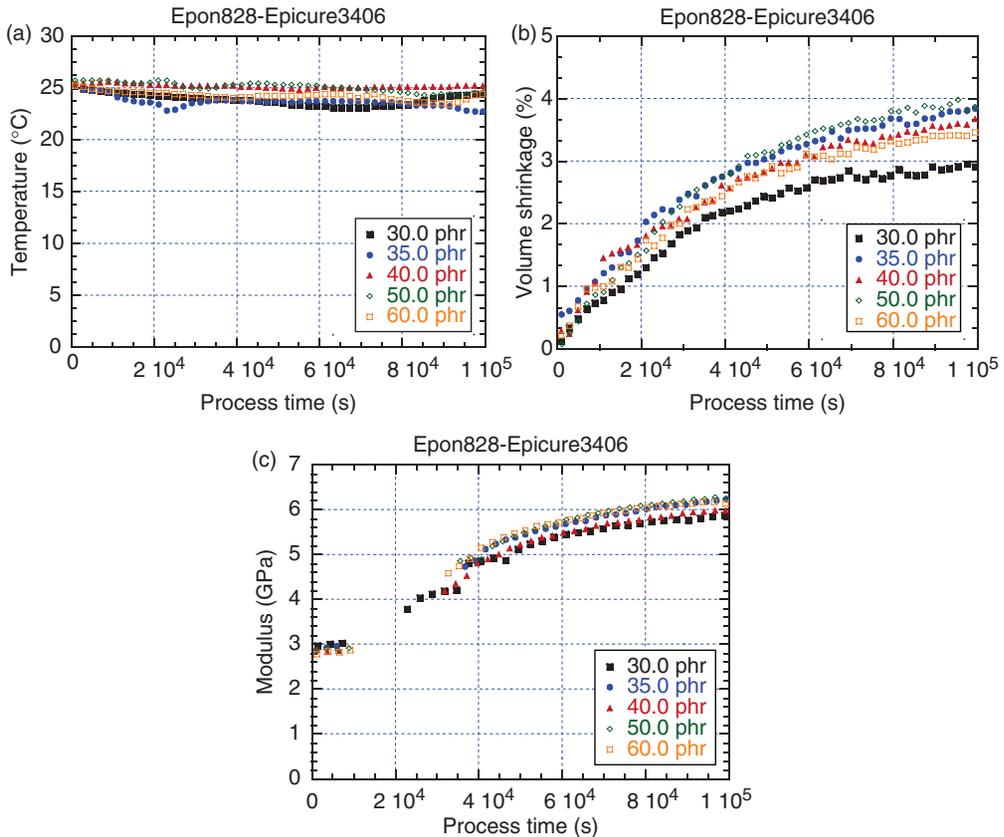


Figure 16. (a) Temperature variation during test on samples with different amounts of hardener (transducer 2) (Epon 828/Epicure 3046); (b) Shrinkage of samples with different amounts of hardener (transducer 2) (Epon 828/Epicure 3046); (c) Modulus variation in samples with different amounts of hardener (transducer 2) (Epon 828/Epicure 3046).

~5000 s into the test. The discontinuity in the curves in Figure 15(c) indicates a loss of the middle pulse represented in Figure 3. After a certain amount of time, the pulse returns. The time for this return of the signal is about 45,000 s and varies with the amount of the hardener. For a resin system with 50 phr of hardener, the return time is later. The modulus of the resin system keeps increasing after that. The modulus curves also show that higher amount of hardener gives rise to higher modulus.

Figures 16 show the temperature variation, shrinkage curves, and modulus development curves for samples of Epon 828 resin with different amounts of hardener (Epicure 3046), but tested with the more powerful transducer 2. The temperature and the shrinkage curves show very similar trends when compared to the results obtained with transducer 1. The modulus curves also show that higher amount of hardener gives rise to higher modulus. However, the modulus curves show a discontinuity at about 10,000 s into the test. After a certain amount of time, the signals return. The time for this return of the signal varies with the amount of the hardener. Also, the signal is lost later and reappears sooner with transducer 2 than with transducer 1, showing that the more powerful UT is more useful. This is reflected in a later time for losing the signals (10,000 s for transducer 2 as compared to 5000 seconds for transducer 1) and the signal return times being earlier (25,000 seconds as compared to 45,000 s).

Shrinkage Versus Degree of Conversion

Since volumetric shrinkage of the resin depends to a large extent on the curing of the resin, it is interesting to relate the resin shrinkage to the degree of conversion (degree of cure of the resin). The degree of cure of the resin was determined using a Differential Scanning Calorimeter DSC/Q10 from TA Instruments. The data were obtained using nitrogen atmosphere and a temperature rate of 10°C/min.

DSC curves of the Epon828-Epicure3046 with different amounts of the hardener are shown in Figure 17. There is some variation in the shapes of the heat flow curves (Figure 17(a)) for different amounts of hardener. Heat flow coming out from samples with

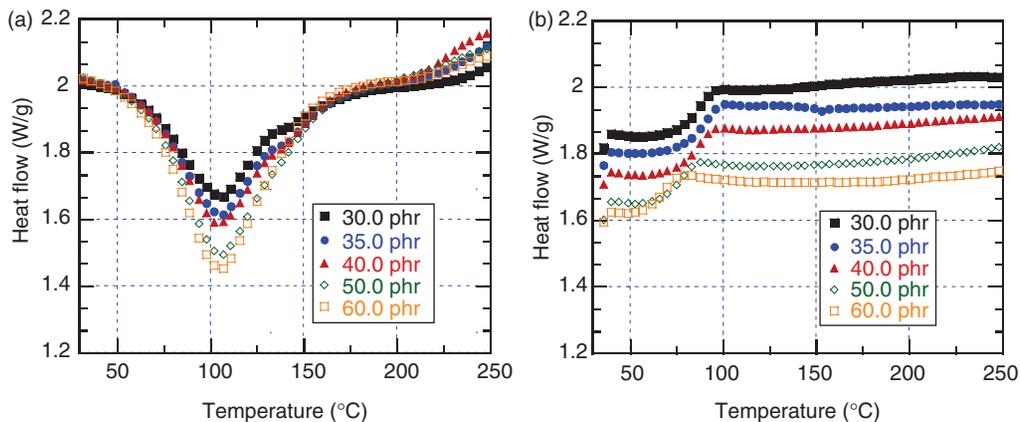


Figure 17. DSC curves of the Epon828-Epicure 3046 with different amounts of hardener, (a) first heating, (b) second heating (Epon 828/Epicure 3046).

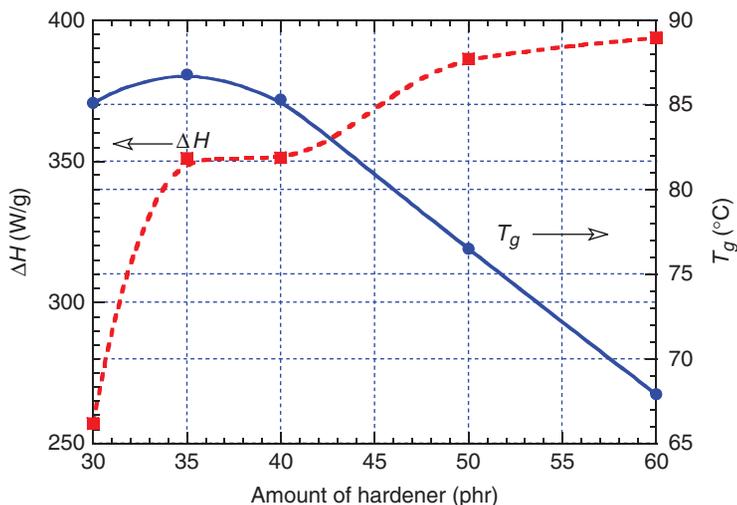


Figure 18. ΔH and T_g for Epon828-Epicure3046 with different amounts of hardener (Epon 828/Epicure 3046).

larger amounts of hardener is more than from samples with smaller amounts of hardener. This may be because when the amounts of hardener increase, the numbers of primary and secondary amines increase. All of the epoxide groups would have reacted with either active primary or secondary amine when the amount of hardener is more than 35 phr and the reaction would have been faster. However, the reaction is more complex with smaller amounts of hardener. There is a shoulder on the DSC curves at higher temperature (150°C .) when the amine is <40 phr (30 phr and 35 phr). This shoulder is clearer for smaller amount of hardener. This may be explained by the reaction between epoxide groups and hydroxyl groups to form ether links after the amines have been consumed.

Figure 18 shows the relation of heat flow ΔH and T_g with different amounts of hardener. With increasing of amount of hardener, heat flow of sample increased. T_g of samples increased and reached a maximum at around 35 phr of hardener, but decreased when more hardener is present. This can be explained by the fact that with larger amounts of hardener (more than 35 phr), there are more residual amines in the cured resin system, which results in more dangling ends and this in turn gives a lower T_g .

Isothermal DSC test at room temperature was carried out up to 100,000 s. The heat flow from these tests was used to calculate the conversion and compare with the shrinkage results. It was assumed that after 100,000 s, both volume shrinkage and DSC conversion reached the value of 1. The comparison of the shrinkage development (data from transducer 2) and the conversion (degree of cure) is shown in Figure 19. It can be seen that both the DSC conversion curves and the shrinkage curves follow the same trend at 30 and 40 phr of Epicure 3046. For 50 and 60 phr of Epicure 3046, there is a little difference in these two curves. The initial slopes of both shrinkage and DSC conversion curves are very similar. However, after about 12,000 s (200 min), the degree of conversion increases at a faster rate than the shrinkage. This goes on until about 84,000 s (1400 min) where the conversion rate tapers off such that both the degree of shrinkage and degree of conversion reach maximum at the same time.

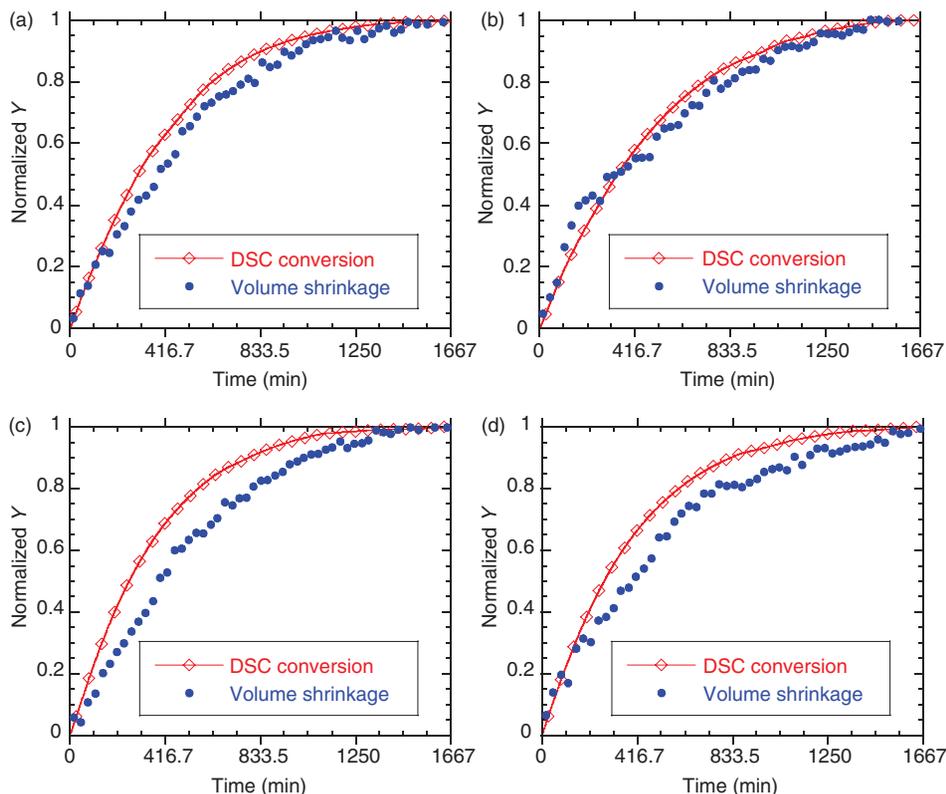


Figure 19. Relation between DSC conversion and the volume shrinkage of Epon828-Epicure 3046: (a) 30 phr, (b) 40 phr, (c) 50 phr and (d) 60 phr.

DISCUSSION

The results presented above show that the PSM can be used to extract the following characteristics of the resin system:

Shrinkage Development

Shrinkage can be determined over the entire curing process. The shrinkage development can be correlated to the degree of conversion in the material. It is important that the temperature of the system remains constant, otherwise there can be some difference between shrinkage and conversion and this difference varies for different resin systems. This is because conversion relates only to a chemical process, whereas volumetric shrinkage includes both chemical and physical effect (such as thermal expansion or contraction).

Modulus Development

The discontinuities shown in Figures 15(c) and 16(c) present interesting indication of the modification of the internal structure of the material. Some possible phenomena such as

phase transformation may take place and is reflected in the time of signal lost to the time of signal reappearance. As such the PSM system may be used to study these phenomena.

The history of shrinkage depends on the temperature history of the sample. In the above examples, increase in temperature results in some form of expansion of the material. The effect of chemical shrinkage can be separated from the physical expansion by holding the temperature of the sample constant. For this condition of constant temperature, the rate of shrinkage can be obtained using the slope of the curve of shrinkage versus time. This slope depends on the composition of the resin system, e.g., the amount of catalyst, inhibitor, promoter, etc.

The PSM system is simple to set up and to operate. It does not require pressurization. The PSM system therefore may provide a simple and accurate method for monitoring volume change and modulus development of many reactive resin systems.

CONCLUSION

A new instrument (PSM) has been developed to monitor the development of shrinkage and modulus of thermoset resin systems while they are curing. Values of shrinkage and modulus for one resin system are presented.

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