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Thermochimica Acta 417 (2004) 115–118

thermochimica acta

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# Real-time measurement of resin shrinkage during cure

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Received 28 July 2003; received in revised form 22 December 2003; accepted 25 December 2003

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**Abstract**

This paper describes a method for in situ determination of shrinkage during cure of thermosets using dynamic mechanical analysis (DMA) instrumentation. The measurement technique correlates shrinkage with gelation so that accumulated stress in the cured system can be assessed. Measurements at elevated temperature are possible. The technique can be adapted to anisotropic shrinkage in systems, such as fiber-reinforced composites, by selection of appropriate sample geometry.

*Keywords:* Shrinkage; DMA; Thermoset

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## 1. Introduction

Shrinkage during cure of thermosetting resins is a well known phenomenon with potentially serious consequences, depending on the application of the material. The consequences of shrinkage include void formation, stress cracking, misalignment of optical components, damage to stress-sensitive inserts, poor adhesion, delamination and warping [1]. These effects can cause failure in adhesives, composites, dental, medical, and electrical potting applications. Among the causes for shrinkage is the reduced distance between molecules as they form crosslinks during the cure process. In addition, the molecules of a semicrystalline polymer may pack better than molecules of an amorphous monomer.

Several approaches are available for measuring cure shrinkage. Some measure volume change, such as those based on a capillary dilatometer, pycnometer, or direct measurement of sample dimensions. Others measure a linear shrinkage and make various assumptions to arrive at a volumetric shrinkage, such as those curing a sample in a trough, or using a thermomechanical analyzer (TMA) or compliant diaphragm. With a capillary dilatometer, the body is filled with the uncured material, then surrounded with an immiscible fluid, such as mercury or water which extends into the graduated capillary attached to the bulb [2,3]. The change in volume of the resin is recorded by noting the change in height of the fluid in the capillary. Similarly, a pycnometer can be used to measure the change in volume of the sample during cure [4]. In that case, the instrument has two connected chambers of known volume. The sample is placed in one of the chambers, which is then evacuated. The sample volume is calculated via Boyle's Law from the change in pressure when a gas is allowed to enter the sample chamber from the other chamber. In some cases, it may be possible to measure sample dimensions directly before and after curing. For example, the volume of a solid powder molding compound can be measured directly before and after curing [5]. A similar approach measures the volume of a sessile drop of resin before and after curing, using a calibrated vision system [6].

Techniques measuring linear shrinkage include those curing a sample in a trough, or using a (TMA) or compliant diaphragm. The ASTM D2566 method uses a hemicircular trough 25.6 cm long having a radius of 1.27 cm [7]. The test result is the amount of shrinkage in the axial direction, corrected for thermal expansion effects when elevated temperature is required for cure. To the degree that the sample surface is prevented from moving freely away from the walls of the mold, the linear shrinkage measured by this test may be less than the expected value of one-third of the volumetric shrinkage. Bair et al. have described an approach using a thermomechanical analyzer to measure change in cure shrinkage in a sample sandwiched between glass plates [8]. The TMA instrument gives a precise measurement of the thickness of the glass/sample sandwich as it cures. Correc-

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doi:10.1016/j.tca.2003.12.027

tion for thermal expansion effects would be required for a system cured at elevated temperature. Bair, et al. show that for a sample having a large ratio of area to thickness, essentially all of the volumetric shrinkage occurs in the axial direction. Another approach for measuring axial shrinkage in a thin sample uses a compliant disc sitting on one surface of a sample confined within a brass ring on a microscope slide [9,10]. In this technique, cure shrinkage is calculated from the deflection of coverslip placed on top of the sample.

This paper demonstrates how to use a dynamic mechanical analysis (DMA) instrument to obtain shrinkage information while simultaneously measuring shear modulus during cure of a thermosetting resin. By this method, it is possible to obtain shrinkage data and approximate gel time from a single experiment. This approach takes advantage of the capability of the DMA instrument to adjust the gap in a parallel plate fixture (i.e. sample thickness) automatically to maintain the axial force on the sample at a preset level. Data are reported for an unfilled commercial epoxy under various conditions and compared with data obtained using a pycnometer.

## 2. Experimental

For the purpose of demonstrating this measurement method, samples of a commercial two-part epoxy adhesive, were prepared following the vendor's recommendation. The material is an amine-cured bisphenol A epoxy with no filler (Masterbond Inc., Hackensack, NJ). This adhesive system cures in 24 h at room temperature, and cure can be accelerated by heating.

Measurement of rheological properties was carried out using a Rheometric Scientific RDA III DMA with an 8-mm diameter parallel plate fixture. Initial sample thickness was in the range of 0.5 mm. Shear modulus was measured at 10 rad/s and followed over time. This instrument will adjust the gap between parallel plates to maintain a fixed compressive or tensile load on the sample while it is applying an oscillating shear displacement to one plate and measuring the torque on the other plate. Shrinkage during cure was measured by monitoring change in sample thickness, which the instrument adjusts during the test in order to maintain $0 \pm 1$ g axial force on the sample. The calculated shrinkage of the sample was based on the change in gap between the parallel plates (i.e. sample thickness) during the test using the equation below:

$$\% \text{ shrinkage} = \frac{L - L_0}{L_0} \times 100$$

where $L$ is the gap at a particular time and $L_0$ the initial gap. These measurements were made at room temperature and at 65 °C. In addition, the approximate gel point was taken as the crossover point of $G'$ and $G''$ This point is somewhat dependent on the measurement frequency.

Comparison of this measurement method with a more traditional approach was made by measuring the volume of a sample of the same material as it cured at room temperature using a Micromeritics AccuPyc 1330 helium pycnometer. This instrument has two connected chambers of known volume. The sample is placed in one chamber, which is then evacuated and back-filled with helium. The volume of helium is determined by transferring the gas to the other evacuated, empty chamber and measuring the change in pressure of the gas. The volume of the sample is then calculated from the difference in the volume of the chamber with and without the sample. The measurement is automatically repeated until three determinations give

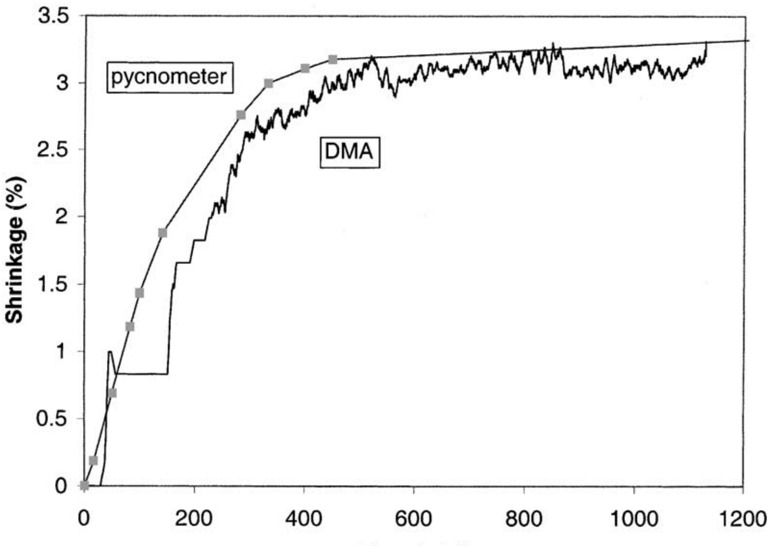

Fig. 1. Shrinkage curves by pycnometer and by dynamic mechanical analysis.

the same volume for the sample. For this measurement, the sample was placed in the sample cup that had been lined with aluminum foil. Measurements of the sample volume were made at regular intervals under ambient conditions.

## 3. Results and discussion

A typical method for measuring volumetric shrinkage of resins has been pycnometry [2]. This method measures total

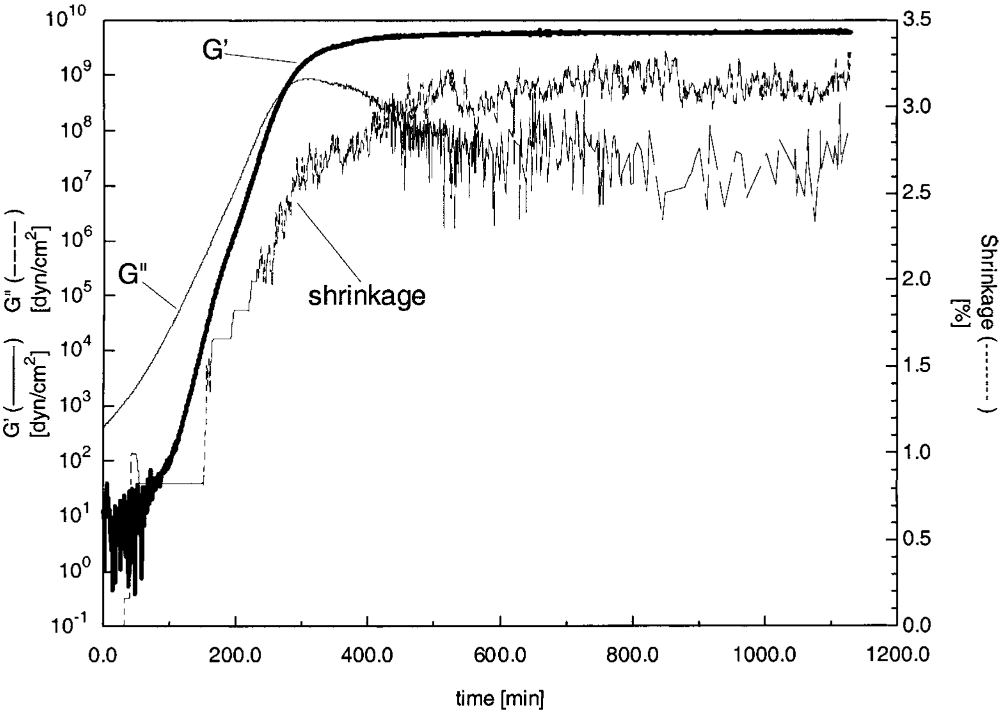

Fig. 2. Shrinkage curve (dotted) and moduli ($G'$, thick solid line; $G''$, thin dashed line) at room temperature.

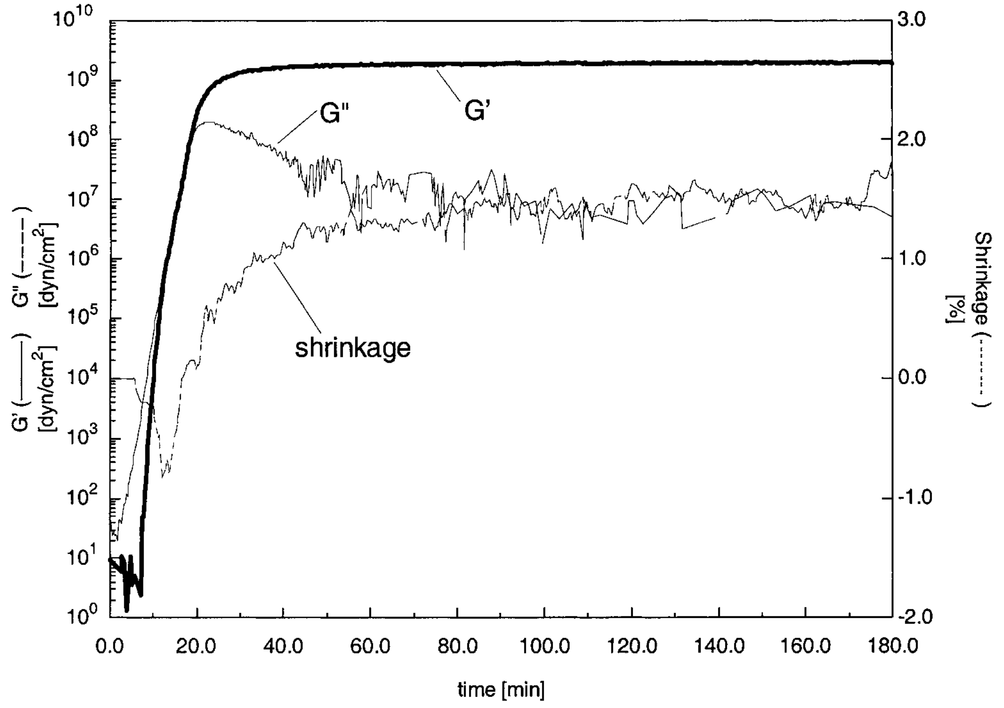

Fig. 3. Shrinkage curve (dotted) and moduli ($G'$, thick solid line; $G''$, thin dashed line) at 65 °C.

change in volume, as opposed to the linear shrinkage obtained from the DMA. Comparison of the results obtained by the two methods is shown in Fig. 1. The curves show good agreement between the two methods. Other workers have shown that the linear shrinkage measured in a thin sample having a large area typically gives good agreement to a measurement of volumetric shrinkage of the same material [8–10].

An advantage of measuring shrinkage by DMA is the ability to monitor shrinkage concurrently with monitoring the mechanical properties of the material. Thus, one can monitor viscosity and shear modulus of the resin, and thereby determine the approximate gel time and shrinkage all in one experiment. When a thermoset formulation reaches the gel point, there is a polymer network formed through the entire sample. Up to that point, the components can flow, so that it is typically assumed that the polymer can adjust to shrinkage before gelation without stressing the material. Only the shrinkage that occurs after the gel point is considered important for determining stress on embedded or attached components because of restricted flow of the components after gelation. Fig. 2 shows the mechanical properties of the resin obtained in the same experiment with the shrinkage curve shown in Fig. 1. The data indicate an approximate gel point of 276 min. For this material, the shrinkage was 2.5% up to the gel point and a total of 3.2% when the material was fully cured. That would suggest that this material would have less stress in the cured material than a composition having most of the shrinkage after gelation.

The ability to conduct this measurement at some temperature other than ambient temperature is another advantage of using the DMA for this measurement. Many thermosets are cured at elevated temperature, making it impossible to use the pycnometer to measure shrinkage while the reaction is proceeding. Fig. 3 illustrates the shrinkage behavior observed in this system when cured at 65 °C. For this measurement, the fixture gap was set to zero after the system had equilibrated at 65 °C, then the sample was applied to the fixture, and the test was conducted. The expansion shown on the curve initially was presumably from the fixture returning to 65 °C after being opened while the sample was inserted. The total shrinkage observed was 2.8% under this condition, compared to 3.2% at room temperature. Note that less of the shrinkage occurred before gelation at 65 °C (1.2% out of 2.8%) than at room temperature. That observation could have importance for choosing process conditions when using this material.

## 4. Conclusions

In situ determination of shrinkage during cure of thermosets by dynamic mechanical analysis has been demonstrated. The measurement technique correlates shrinkage with gelation so that accumulated stress in the cured system can be assessed. Measurements at elevated temperature are possible. The technique can be adapted to anisotropic shrinkage in systems, such as fiber-reinforced composites, by selection of appropriate sample geometry.

## Acknowledgements

The assistance of Dr. S.R. Gurkovich with the pycnometer measurements is gratefully acknowledged.

## References

[1] H. Lee, K. Neville, Handbook of Epoxy Resins, McGraw-Hill, New York, 1967, pp. 6-29–6-31.
[2] N. Bekkedahl, J. Res. Natl. Bur. Stand. 42 (1949) 145.
[3] J.P. Armistead, A.W. Snow, Polym. Mater. Sci. Eng. 66 (1992) 457.
[4] H. Lee, K. Neville, Handbook of Epoxy Resins, McGraw-Hill, New York, 1967, pp. 17-11–17-15.
[5] K. Oota, M. Saka, Polym. Eng. Sci. 41 (2001) 1373.
[6] A.J. Hudson, S.C. Martin, J.K. Spelt, Trans. ASME 124 (2002) 352.
[7] ASTM Test Method D2566, Standard Test Method For Linear Shrinkage Of Cured Thermosetting Casting Resins During Cure (Discontinued 1993 No Replacement), ASTM International, West Conshohocken, PA, 1986.
[8] H.E. Bair, M.L. Schilling, V.L. Colvin, A. Hale, N.J. Levinos, Proc. North Am. Therm. Anal. Soc. 28 (2000) 554.
[9] D.C. Watts, A.S. Marouf, D. Heindl, Proc. SPIE 4771 (2002) 19.
[10] D.C. Watts, A.J. Cash, Dental Mater. 7 (1991) 281.