

A Simple Dilatometer for Thermoset Cure Shrinkage and Thermal Expansion Measurements

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SYNOPSIS

A simple capillary and bulb mercury dilatometer designed for specific volume measurements on thermoset resin systems during the curing reaction and as a function of temperature is described. The design, calibration, operation, data treatment, and error analysis are presented in detail, with data on the bisphenol A dicyanate resin system used as an example. Particular attention is directed at experimental difficulties such as monomer/prepolymer degassing, filling the dilatometer under vacuum, adhesive distortion of the curing resin on the dilatometer bulb, and the dilatometer bulb to capillary connection problem. © 1994 John Wiley & Sons, Inc.[†]

INTRODUCTION

The need for volume change information accompanying thermoset cure and thermal expansion/contraction connects fundamental chemistry with practical applications and impacts on processing, mechanical properties, interfacial adhesion, internal stress, and fatigue of these materials. Processing, especially with molds, places a threshold on the amount of cure and thermal shrinkages that vary significantly with cure temperature. Mechanical properties depend on the amount of free volume that may be locked in via chemical structure and thermal quenching. Interfacial adhesion may correlate with a thermal expansion mismatch and a postvitrification volume change during cure. Physical aging and fatigue may, likewise, correlate with small volume changes.

In this work, we are primarily concerned with volume changes accompanying the cure reaction and thermal expansion of cyanate thermoset resins. This report is a detailed account of customizing the design of a dilatometer to make such measurements. Thermoset polymers present somewhat unique challenges in that the material starts as a viscous liquid and

transforms into a rigid solid with excellent adhesive properties. It is this characteristic that makes these materials useful as composite matrix resins.

Literature reviews on dilatometry may be traced back to an 1894 text by Ostwald,¹ but it is not a very popular topic for modern physical chemistry books. A 1949 review by Bekkedahl² is the most cited reference for experimental detail. A 1973 reference by Wilson and Simha³ also presents very useful experimental information for simple dilatometers. Specific to polymers, reviews in the *Encyclopedia of Polymer Science and Technology*⁴ and *Encyclopedia of Polymer Science and Engineering*⁵ provide good general coverage of dilatometry on polymer systems and, in the former case, of dilatometer design. However, little is said about details of problems unique to thermoset polymers. References 6–9 report dilatometric measurements on thermoset systems, most of which are epoxy. References 4 and 10 contain information relevant to thermoset dilatometry. Comments regarding these references will be made where pertinent individual details are being discussed.

The objective of this report is to describe a simple (i.e., constructible from commercially available glassware with routine glassblowing skills) and versatile dilatometer designed specifically for measurements on thermoset polymers. These measurements include specific volumes of monomers and cured polymers, the volume coefficient of thermal expansions, and the specific volume change of the cure

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reaction. Experimental obstacles such as monomer/prepolymer degassing, filling the dilatometer under vacuum, adhesion distortion by the cured resin on the dilatometer bulb, and the dilatometer bulb to capillary seal will be discussed along with a detailed operational procedure and data workup.

DILATOMETER DESIGN

Features and Obstacles

Parts Description

A drawing of the dilatometer used in this work is presented in Figure 1. It consists of three main parts: a detachable bulb, a graduated precision bore capillary, and a filling apparatus. The bulb is constructed from a 18/9 standard ball joint. The joint is sealed with a rounded end as in the drawing with a mouth to tip length of approximately 32 mm. The sealing should be done so that there is no enlargement in tube diameter or the cured thermoset will not eject through the mouth of the ball joint. This bulb is approximately 2 mL in volume and easily accommodates 1 g of thermoset.

The precision bore capillary (diameter of 1.02 to 1.07 mm and graduated length of 40 cm) with the bend and socket joint at the bottom is obtained commercially (Ace Glass, Vineland, NJ; Volumetric Dilatometer, Catalog Number 6283). With the services of a glassblower, the 12/5 socket joint is replaced with an 18/7 standard socket joint (preferably from the same vendor from whom the bulb ball joint was obtained), and a 10/30 standard taper inner joint is attached to the upper end for connection to the filling apparatus. The volume of the capillary end to socket joint connection should be minimized to preserve the accuracy of a good mercury to polymer volume ratio which is 2 : 1 in the present case.

The filling apparatus is constructed from a polytetrafluoroethylene valve (Kontes, Vineland, NJ; PTFE Valve with bent sidearms, 4 mm bore, Catalog Number 826620-0004), a 35 mL bulb, a 10/30 standard taper outer joint, and a vacuum manifold connecting joint (in this case a standard taper 12/30 inner joint). The PTFE valve allows for vacuum storage of the mercury in the bulb and for control of the mercury transfer rate when filling the dilatometer. The bends in the sidearms of the PTFE valve are well suited for straight-on connections to the bulb and capillary connecting joint. The manifold connecting joint may connect vertically beneath a vacuum manifold or to flexible vacuum tubing. For the vertical manifold connection, the angle of this joint is determined by an orientation that will

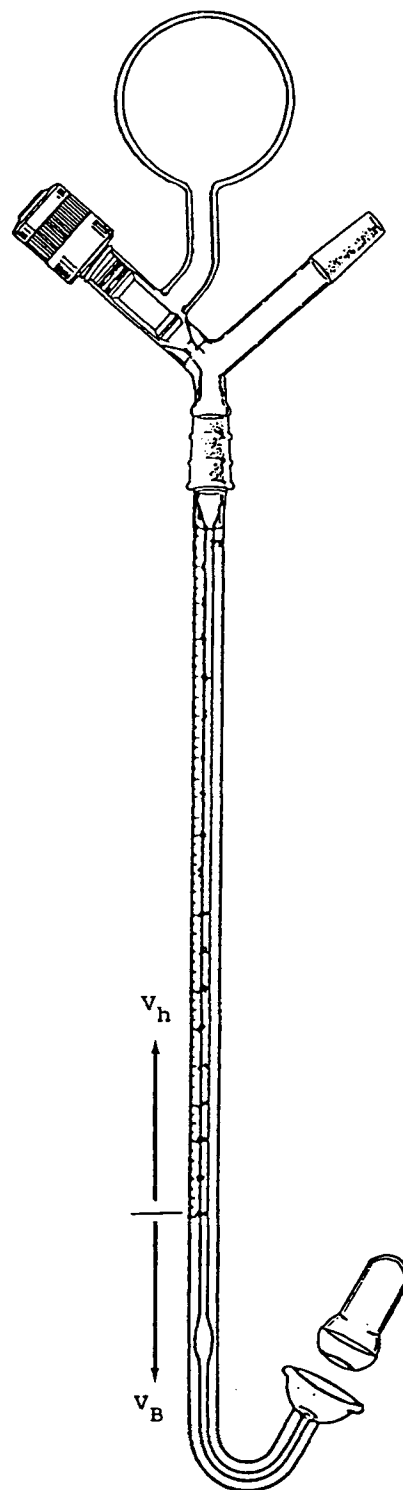


Figure 1 Dilatometer design used in this study. The zero line indicated demarcates the dilatometer bulb volume, V_B , from the capillary volume, V_h .

permit dropwise quantities of mercury to pass through the valve and slide down the capillary to fill the dilatometer bulb with relative ease. This ori-

entation is closely parallel to the top sidearm of the valve and can be finely adjusted with a torch until the best compromise angle is found. The capillary connecting joint may be rotated to orient the dilatometer bulb for the mercury-filling operations. This joint should also be reinforced with a plastic clamp or springs/hooks during these operations.

Adhesion of Thermoset to Dilatometer Bulb

Because most thermosets have very good adhesive properties, two serious dilatometry problems arise as a consequence of the resin to bulb adhesion produced during the curing reaction. Stress, both internally on the thermoset and externally on the dilatometer bulb, is generated as the specific volume of the thermoset changes relative to the volume of the bulb. This stress distorts the volume measurement by perturbing the thermoset from its equilibrium state, generating microvoids, and deforming the bulb. In many cases when the bulb wall is not thick enough to withstand the stress, the result is catastrophic. The second problem is ejection of the cured thermoset after the measurement and preservation of the calibrated bulb. Damage-free detachment of the resin from the bulb is frequently impossible.

In the literature, two techniques are used to address this resin adhesion problem. One method is to encapsulate the monomer or prepolymer in a flexible thin film bag made of poly(vinyl fluoride),⁶ polycaprolactam,⁶ or emulsoid rubber,⁹ which is subsequently placed in the dilatometer bulb. The contribution of the bag to the volume measurement must, of course, be corrected for if not negligible, and the bag must be stable and inert under conditions of the measurement. The other method involves coating the interior of the bulb with a "parting agent" composed of silicone vacuum grease that was reported to be unsatisfactory.⁷ The bag method has the convenience of a facile removal of the resin after the measurement but the complication of procurement, filling, sealing, invoking a correction factor, and stability limitations (chiefly temperature).

The approach in this work was to identify a Pyrex glass surface treatment that prevents adhesion of curing thermoset resins. This has the advantage of eliminating a correction factor in the dilatometer measurement. The testing involved curing a 1 g quantity of Epon 828 (Shell Chemical Co.) in a 10 × 75 mm surface treated Pyrex tube and determining that the cured resin plug could be removed by simple inversion and tapping. The surface treatment products tested included (1) MS122 (PTFE solids spray

on mold release agent, Miller-Stephenson Chemical Co., Danbury, CT), (2) MS136 (fluorocarbon spray on mold release agent, Miller-Stephenson Chemical Co., Danbury, CT), (3) Frekote 700 (proprietary resin release spray on release agent, Frekote, Seabrook, NH), (4) 3M Silicone Lubricant (Siloxane mold release spray, 3M Company, St. Paul, MN), (5) perfluoroparaffin wax (Fisher Chemical Co., Silver Spring, MD), (6) Glassclad 18 (monomeric octadecylsilanol siliconizing reagent, Petrarch Systems, Bristol, PA), and (7) Glassclad 6C (chlorine terminated polydimethylsiloxane telomer siliconizing reagent, Petrarch Systems, Bristol, PA). Only the Glassclad 6C passed the testing. Failures ranged from catastrophic implosion to resin cracking to nonrelease. The Glassclad 6C had the further advantage that it could be cycled many times without losing its release properties. However, a treated surface should not be contacted with concentrated nitric acid, which is used to clean mercury residues from the capillary. Nitric acid contact causes the surface to become opalescent and lose its release properties. The precision bore capillary component of the dilatometer should not be surface treated. The surface treatment may be removed by brief contact with 30% hydrofluoric acid, but such treatment makes recalibration necessary.

Bulb to Capillary Connection

Since the thermoset cure results in a liquid being transformed to a nonmelting, insoluble solid, the dilatometer used to monitor the cure reaction must be designed for removal of the cured resin. The alternatives are a burn-away oxidation or an acid digestion, both of which can be very messy and time consuming as well as detrimental to a release surface treatment. For resin removal, the mechanical requirement is a wide-mouth connection on the dilatometer bulb. An operational requirement is that the connection be vacuum tight for the degassing and filling procedures and stable at measurement temperatures. Further, if variable temperature measurements are being made, the connection should not contribute to the volume measurement.

To make this connection, an O-ring⁶ and standard taper joint^{3,10} have been used. The O-ring has the appeal of being a greaseless vacuum tight mechanical seal. Restrictions are: (1) the O-ring must totally compress within its groove such that the rigid surfaces of the connection are intimately in contact and remain so at elevated temperatures in order not to add to the volume of the bulb, and (2) the O-ring be stable and not out gas at resin cure temperatures

that may be as high as 250°C. The standard taper joint, if made of ground glass, requires grease for a vacuum-tight seal. While the vacuum grease film between the joint surfaces is easily thin enough not to perturb the bulb volume, its spreading when the joint surfaces are brought into initial contact can result in a milligram or submilligram quantity migrating to the inner edge of the joint contact area. This can translate into a 10^{-3} mL/g specific volume error.

The initial approach in this work is to employ a standard ball and socket joint for this connection. The vacuum grease problem still exists (*vide infra*), but the ball and socket joint dimensions are such that less volume is added to the bulb compared with the taper joint. Current efforts to circumvent the vacuum grease problem involving trial of an O-ring ball joint and use of PTFE cladding on the ball joint have been unsuccessful.

Degassing

Residual solvent, dissolved air, occluded air, and volatile byproducts of initiators are very detrimental to the specific volume measurement, especially at elevated cure reaction temperatures. For example, 1 μ g of volatile impurity at a 200°C cure temperature can produce a 1 mm diameter bubble with a volume of 0.0005 mL. A very brief reduced-pressure stirred degassing of the monomer or resin prepolymer at the cure temperature followed by transfer to the dilatometer and a second very brief degassing within the dilatometer before filling with the confining fluid is good insurance against traces of volatiles disrupting the volume measurement. The severity of the degassing conditions is dependent on the vigor of the cure reaction and the importance of initial cure reaction data points.

Dilatometer Confining Fluid

Mercury offers many advantages as the choice for the confining liquid. These include: (1) total insolubility in and nonreactivity with the resin, (2) stability, nonvolatility, and very accurately known expansion over the temperature range of interest, and (3) a large density that enhances precision of the dilatometer calibration. This large density has the disadvantage that the dilatometer bulb must be inverted during filling and during operation to prevent the molten monomer or prepolymer from plugging the capillary. Silicone oil has also been used as a confining fluid.⁹

Filling under Vacuum

For simple dilatometers using mercury as the confining fluid, the filling apparatus consists of a three-way stopcock fixed to the top of the capillary that alternately connects the dilatometer to a vacuum source and a mercury reservoir.^{2,3} More complicated dilatometers fill from beneath the capillary, which makes for better control of the filling operation but complicates the weighing and heating operations. The PTFE valve arrangement in Figure 1 has the advantages of fine control of the mercury dispensing rate, has no grease to contact with the mercury, and allows for facile return of the mercury from the capillary to the reservoir.

Quantitative Aspects

Basic Equation

For calculation purposes, the volume of the dilatometer is divided into contributions from two components; that of the capillary, V_h , and that of the bulb, V_B . The demarkation between the two is the zero line on the capillary graduation as indicated in Figure 1, and the capillary volume is determined by the height of the mercury in the capillary. The volume of the polymer in the bulb, V_p , is then the difference between the measured sum of the capillary and bulb volumes and the volume occupied by the mercury, V_{Hg} .

$$V_p = (V_h + V_B) - V_{Hg}$$

Keeping the representative quantities in the same order, this equation achieves a more useful form expressed as a polymer specific volume, V_{sp} , with the capillary volume expressed as a cylinder and with thermal expansion correction terms for Pyrex glass and mercury added in a manner similar to that done in Ref. 2.

$$V_{sp} = (1/W_p)[(\pi(d/2)^2h + V_B) \times (1 + \beta_{py}(T - 25)) - W_{Hg}(V_{sp,Hg}(1 + \beta_{Hg}T))]$$

Where W_p (g) is the mass of resin in the dilatometer, d (cm) is the dilatometer capillary diameter, h (cm) is the height of mercury in the dilatometer capillary, V_B (cm³) is the calibrated volume of dilatometer bulb, β_{py} (0.000010°C⁻¹)² is the Pyrex glass volume coefficient of thermal expansion at 25°C, T (°C) is temperature of dilatometer bulb, W_{Hg} (g) is the mass of mercury in the dilatometer, $V_{sp,Hg}$ (0.073554 cm³/g)² is the mercury specific volume at 0°C, and β_{Hg} (0.000182°C⁻¹)¹¹ is the mercury volume coefficient of thermal expansion at 0°C.

The circular cross-section of the capillary is determined by the dilatometer calibration (see following section), and the quantity $\pi(d/2)^2$ is replaced by the capillary calibration constant, c . Also, if the capillary emerges from the temperature control bath, a stem correction similar to that used for thermometers for the differential thermal expansions of the Pyrex glass and mercury should be made. These expressions are as follows:

$$c = \pi(d/2)^2$$

$$\text{stem correction} = c(\Delta h)(\beta_{\text{Hg}} - \beta_{\text{py}})(\Delta T)$$

where Δh is the capillary length above the temperature bath and ΔT is the temperature difference between the bath and the midpoint of Δh (close to room temperature). Incorporating these expressions into the specific volume equation gives the following working equation for the dilatometer.

$$V_{\text{sp}} = (1/W_p)[(ch + V_B)(1 + \beta_{\text{py}}(T - 25)) + c(\Delta h)(\beta_{\text{Hg}} - \beta_{\text{py}})(\Delta T) - W_{\text{Hg}}(V_{\text{sp,Hg}}(1 + \beta_{\text{Hg}}T))] \quad (1)$$

The calibration establishes the dilatometer values of c and V_B , and the values of W_p , W_{Hg} , h , and T are taken as data during the experiment with the resin.

Selection of Bulb Size, Capillary Size, and Mercury : Polymer Volume Ratio

In designing a dilatometer, the magnitude of the volume change is a key consideration for the selection of precision bore capillary and bulb sizes. For temperature-dependent measurements, the volume ratio of confining fluid to polymer has a strong effect on the precision. The thermal expansion of the fluid may also need to be considered. As a guide for such design considerations, the following equation has been found to be useful.

$$\frac{\Delta V_p}{V_p} = \frac{\pi(d/2)^2 \Delta h}{\phi V} - \beta_{\text{Hg}} \Delta T \quad (2)$$

where $\Delta V_p/V_p$ is the fractional change in resin volume, d (cm) is the diameter of dilatometer capillary, Δh (cm) is the length of capillary to accommodate volume change, ϕ is the volume fraction of resin in mercury-polymer combination, V (cm³) is the volume of dilatometer, β_{Hg} (0.000182°C⁻¹) is the mercury volume coefficient of thermal expansion, and ΔT (°C) is the temperature range for the dilatometer

measurement. Equation (2) may be used to calculate the magnitude of volume change a dilatometer with particular design characteristics can accommodate. The first term on the right of the equal sign contains the dilatometer's critical dimensions and the effect of the confining fluid to resin volume ratio. The second term accounts for the thermal expansion of the confining fluid over the temperature range of the measurement. As an example, consider a dilatometer with a 1 mm diameter capillary, a 20 cm effective length, 3 mL volume, a 2 : 1 mercury to resin volume ratio ($\phi = 0.33$) and a thermoset that cures at 200°C ($\Delta T = 175^\circ\text{C}$). Then, $\Delta V_p/V_p = 0.16 - 0.03 = 0.13$ or about a 13% prepolymer volume change. If the polymerization process causes shrinkage, then, after reaching cure temperature equilibrium, ΔV_p becomes negative, and the limit of shrinkage measurable is 19% because this effect is opposite to the thermal expansion of the mercury.

CALIBRATION

The dilatometer is calibrated for two parameters, the capillary constant, c , and the dilatometer bulb volume, V_B . The capillary constant is the volume per unit height (or circular cross section assuming a cylindrical shape) of the capillary. The dilatometer bulb includes the capillary volume up to the point where the graduated markings begin. To obtain these calibration parameters the dilatometer is filled with mercury (see following section) to various heights in the capillary, and the mass and capillary height of the mercury are recorded. The mass measurements of mercury are converted to volumes via eq. (3), and a plot of volume vs capillary height is constructed (Fig. 2).

$$V = W_{\text{Hg}}(V_{\text{sp,Hg}}(1 + \beta_{\text{Hg}}T)) \quad (3)$$

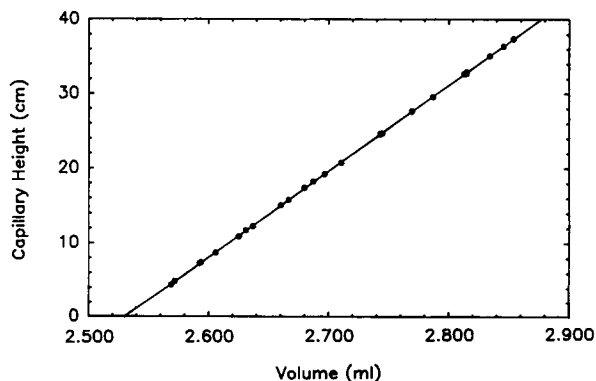


Figure 2 Dilatometer calibration plot to obtain capillary constant and dilatometer bulb volume.

The slope and intercept of the calibration plot yield the respective values for c and V_B . The uniformity of the capillary along its length is reflected in the linearity of the plot. In the example of Figure 2, the respective values of c , V_B , and the linear correlation coefficient are 0.0086696 mL/cm, 2.5293 mL, and 0.999997. A capillary diameter of 0.1051 cm may be calculated from the value of c and is within the precision range (1.02–1.07 mm) quoted by the manufacturer.

OPERATION

Cleaning

Cleaning is recommended if the dilatometer is newly constructed or mercury residues are observed adhering to the capillary. For the capillary and filling apparatus the following sequence has been found to work well: concentrated nitric acid to remove mercury residues (with hot air heating if necessary); water rinse, acetone flush, and methylene chloride to remove vacuum grease; 1 : 1 mixture of concentrated nitric and sulfuric acids for trace organic films; distilled water rinse and vacuum drying. If the bulb has been surface treated with siliconizing agent, it should not be contacted with nitric acid but cleans easily with acetone and water rinses.

Bulb Surface Treatment

This treatment involves contacting the inside surface of the dilatometer bulb with a series of solutions. For convenience, the bulb is positioned upright standing in the neck of a vial supported by the larger diameter of the ball joint. The solutions are transferred to and from the bulb with a clean medicine dropper to avoid solution contact with the surface of the ball joint. The bulb is first filled with a 50% hydrofluoric acid solution (J. T. Baker Chemical Co., Phillipsburg, NJ) for 15 s, emptied, and rinsed with distilled water. It is then filled with a 3% NaOH solution for 60 s, emptied, rinsed thoroughly with distilled water, and dried at 110°C for 60 min. After cooling, the bulb is filled with a 5% solution of Glassclad 6C (Petrarch Systems, Bristol, PA) in methylene chloride for 2 min, emptied, and dried at 110°C for at least 20 min before use.

The release properties from this treatment have survived as many as five dilatometer measurements of cyanate resin cure at temperatures approaching 225°C. The treatment is also effective for multiple epoxy cures at 125°C. When the release appears to

be deteriorating, the treatment can be renewed by starting at the NaOH solution treatment in the above paragraph. The calibration is not perturbed by this treatment renewal.

The treatment may be removed by contact with nitric acid followed by lifting off of the clouded film by filling with the 50% hydrofluoric acid. Retreatment can then be done, but recalibration is necessary.

Thermoset Degassing

The degassing conditions depend on the volatility of the thermoset monomer or prepolymer and the curing agent or catalyst. Ideally, the initial cure temperature, usually selected for at least a 2 h reaction time, is used for the degassing, and the vacuum is adjusted to avoid resin component loss. The degassing time is also minimized to minimize thermoset cure conversion.

It had been found advantageous to do the degassing in two stages. In the first stage, 1 to 2 g of monomer or prepolymer in a small round bottom flask is placed in a preheated bath. The resin is magnetically stirred, and the pressure is gradually reduced such that distillation or sublimation does not occur. This is done over a 10 to 15 min period. Because a curing additive has not been added, conversion is not much of a concern. The curing agent or catalyst should be separately degassed if practicable. In the second stage, the appropriate quantity of curing agent or catalyst is added to the molten resin, stirred, and the pressure quickly reduced. Once the previous vacuum is obtained, the stirring is continued for 1 to 2 min. The resin is then rapidly transferred via preheated medicine dropper if necessary to the preweighed dilatometer bulb. It is also possible to degas again after the bulb is connected and the dilatometer evacuated before filling. This last degassing may be helpful if resin crystallization is a problem.

Dilatometer Assembly and Filling

After the resin has been transferred to the bulb and weighed, dilatometer assembly and mercury filling should be done without delay to avoid diffusion of air into the resin. If the resin is a room-temperature flowing liquid, the dilatometer parts (vacuum greased bulb, dilatometer capillary, and clamp) have to be weighed separately for a tare weight before filling with mercury.

Vacuum grease (High Vacuum Silicone Grease, Cat. No. 970V, Dow Corning, Midland, MI) is ap-

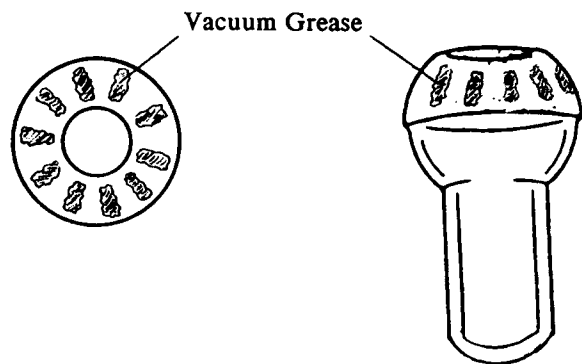


Figure 3 Vacuum grease application pattern on dilatometer bulb ball joint.

plied carefully and sparingly as illustrated in the drawing of Figure 3. The idea is to apply the minimum quantity of grease, positioning it in lines radiating out from 2 or 3 mm just short of the inside edge of the ball joint so that, when the ball is seated into the socket of the capillary, the grease will spread smoothly, displacing air and connecting with adjacent lines. It is very important to avoid excess grease migrating beyond the inside edge of the ball joint and contributing to the specific volume measurement. If the resin is a room-temperature liquid, the bulb must, of course, remain upright at this time to prevent the resin from contacting with the dilatometer capillary. A spring-loaded pinch clamp with a screw-locking device is placed on the joint with the screw-lock tightened with maximum finger pressure. The tight locking of this clamp prevents mercury leakage through the joint during measurements at elevated temperatures.

If the resin is a solid, the tare weight before the mercury addition is now determined. An electronic balance with a draft shield and vertical access to the weighing chamber (Metler AE100) is convenient. A dilatometer holder for the balance pan can easily be made by notching an inverted pair of nested polystyrene coffee cups.

The filling apparatus (with mercury stored under vacuum in the reservoir) is connected to the dilatometer capillary and to the vacuum manifold. This is a flexible hose connection if further degassing is to be done or if the resin is a liquid. With the bulb upright, a final degassing may be done at this time using gentle electric air gun warming. The resin is then solidified (with liquid nitrogen cooling if necessary) while pulling a vacuum of 5×10^{-3} mm or better for at least 5 min. The manifold connecting joint of the filling apparatus is connected vertically beneath a vacuum manifold or, the dilatometer is

simply oriented into this position if a flexible tubing connection has already been made. The capillary to filling apparatus joint should be rotated so that the dilatometer bulb is below the level of the capillary. If there is a liquid resin the bulb, the mercury filling must be started before the resin has had time to warm and flow to the joint connection. The valve to the mercury reservoir is very gradually opened until a very slow trickle of mercury flows. This can be initiated by a gentle tapping on the valve as the Teflon to glass contact becomes weak. The dilatometer should be filled to the first 5 to 10 cm of the capillary height. After closing the mercury valve, a bead of mercury may be setting in the entrance of the capillary. This may be pushed down to join the mercury in the bottom of the capillary by very slowly bleeding air into the manifold. The dilatometer is disconnected from the filling apparatus, and the vacuum grease is thoroughly cleaned off the capillary taper joint prior to weighing the dilatometer.

A small amount of settling (1 to 2 mm drop in the mercury level) occasionally occurs an hour or so after filling. A settling time of 2 h or longer after filling is recommended.

Data Collection

Two types of experiments are conducted: specific volume measurements as a function of cure reaction time and thermal expansion measurements on the monomer/prepolymer and cured thermoset. It is possible to do both on the same sample if the cure reaction is negligibly slow over a sufficient temperature range for enough expansion measurements to be made. This is the case for the uncatalyzed cure of bisphenol A dicyanate (AROCY B-10 monomer, contributed by D. A. Shimp, Rhone-Poulenc, Louisville, KY), and it will be used as an example.

Monomer Thermal Expansion

The dilatometer is clamped vertically above a temperature-controlled bath with the bulb immersed about 1 inch and the immersion depth on the capillary recorded for the stem correction. A thermometer is also positioned with its bulb immediately adjacent to the dilatometer bulb. Equilibration occurs in 5 to 10 min and the temperature and height of mercury in the dilatometer are recorded. The bath temperature is stepped up 5 to 10°C, and temperature-dilatometer data recorded after equilibration. As the melting point of this monomer (82°C) is approached, additional equilibration time is necessary for the fusion process. After the upper end of the

temperature range is reached, measurements are made in the decreasing temperature direction. In this example, the monomer may be supercooled to room temperature extending the temperature range for monomer melt thermal expansion measurements.

Thermoset Cure

The temperature-controlled bath is preheated to the cure temperature (200°C), and the dilatometer and thermometer are immersed and positioned as described above. The cure time and mercury column height are recorded at rapid intervals (1 min) at first, then less frequently as the specific volume change becomes slower. During the cure, mercury can be observed to fill much of the space between the bulb wall and resin plug as the gel point is passed and the resin continues to contract. Eventually, the specific volume becomes constant. Postcure measurements at higher temperatures may be continued.

Cured Thermoset Thermal Expansion

These measurements are made after cooling in the direction of increasing then decreasing temperature as was done above for the monomer.

Dilatometer Emptying and Disassembly

To remove the mercury the dilatometer is reconnected to the filling apparatus, which is connected

to a vacuum via a flexible tube. The dilatometer is evacuated, and the mercury induced to flow back into the reservoir by manually tilting the apparatus. Careful transfer of the mercury can leave the capillary free of mercury beads. The clamp is removed, and the bulb is detached. After cleaning the exterior and joint surface, the resin plug is ejected usually by gentle tapping.

DATA TREATMENT

All data reduction involves conversion of the mercury capillary height readings to specific volumes for which eq. (1) is used. This is programmable into a pocket calculator or minicomputer. The specific volume plotted as a function of temperature or of cure time is illustrated for the cyanate resin in Figures 4 and 5.

The specific volume vs. temperature plot is particularly useful as the volume coefficients of thermal expansion for the crystalline and molten monomer, and cured polymer may be obtained from the slopes (normalized to V_0 , the 0°C volume, i.e., $\beta = (1/V_0)(dV/dT)$) of the plot and the specific volumes of monomer fusion and cure may be obtained from the vertical displacements. For the cyanate resin example, these respective values are $\beta_{M,C}$, $9.5 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$; $\beta_{M,M}$, $6.9 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$; β_P , $1.6 \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$; $\Delta V_f^{82^\circ\text{C}}$, 0.071 mL/g; $\Delta V_{Rx}^{200^\circ\text{C}}$, 0.119 mL/g.

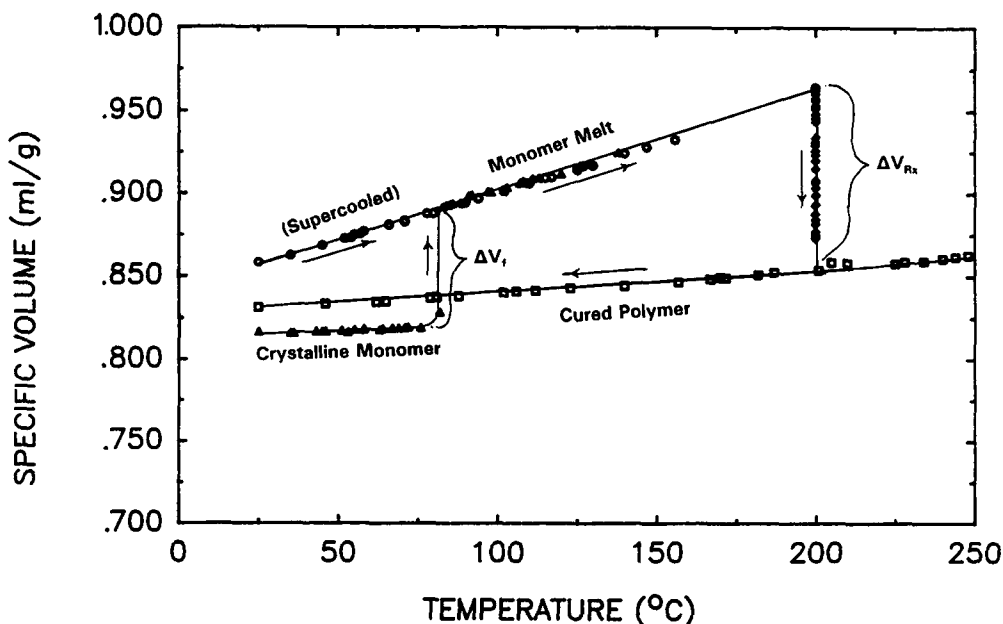


Figure 4 Bisphenol A dicyanate specific volume-temperature data.

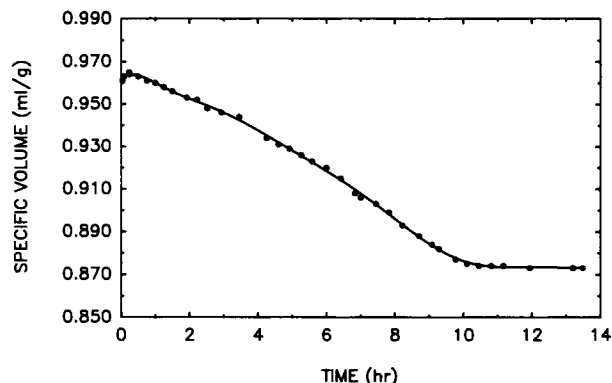


Figure 5 Bisphenol A dicyanate specific volume-cure time data.

Two features of Figure 4 are noteworthy. The data points for the thermoset cure do not show shrinkage extended to the thermal expansion line of the cured polymer. This gap may be due to the space that develops between the dilatometer bulb wall and cured resin plug being too small for the mercury surface to completely penetrate until additional thermal shrinkage occurs after cooling to room temperature. Once having flowed into this gap the mercury surface tension effect does not reoccur on thermal cycling. The second feature concerns the accuracy of the crystalline monomer specific volume. When this monomer crystallizes as a 1 g mass within the dilatometer, the specific volume measured at room temperature is 0.8164 mL/g. This result compares with a buoyancy measurement on a large single crystal 0.7943 mL/g¹² and with x-ray crystal structure results of 0.7874 mL/g¹³ and 0.7819 mL/g¹⁴. The dilatometer specific volume measurement is larger, and a probable cause is voids at crystal grain boundaries of the polycrystalline bisphenol A dicyanate mass.

In Figure 5, the specific volume during cure at 200°C continually decreases for 10 h then levels off at a constant value. This leveling off value should be considered with caution. It does not necessarily mean that cure conversion has stopped nor does it appear to be free of a dilatometer bulb wall effect described in the paragraph above and illustrated in Figure 4. A more meaningful plot is one of specific volume against degree of conversion. This data is obtained from partially cured samples analyzed for cure conversion. Figure 6 displays such a plot for the bisphenol A dicyanate resin with measurements made at 20 and 200°C. It is noteworthy that the 20°C measurement indicates an apparent expansion occurs beyond 60% conversion while the 200°C

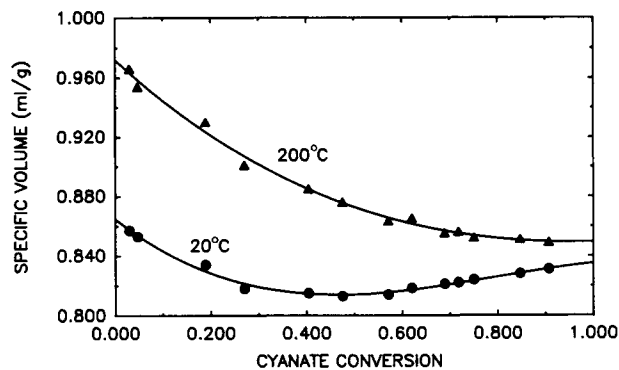


Figure 6 Bisphenol A dicyanate specific volume measurements at cure (200°C) and room (20°C) temperatures as a function of cyanate conversion.

measurement does not indicate an expansion. The minimum at 60% conversion does not represent a volume expansion attributable to the cure reaction but is a consequence of an advancing glass transition temperature with increasing conversion. Data for this effect are illustrated in Figure 7. Thermal expansion has a greater temperature dependence above than below the glass transition. Advancement of cure may cause a small shrinkage, but the increase in glass transition temperature results less “rubbery” shrinkage on cooling and a crossover to an apparent expansion if the volume measurement is made at room temperature. This effect is illustrated in Figure 8.

ACCURACY AND ERRORS

To obtain an assessment of the accuracy of the measurements with the dilatometer described in this report, it is possible to do propagation of errors calculation and check it with a series of repetitive measurements.

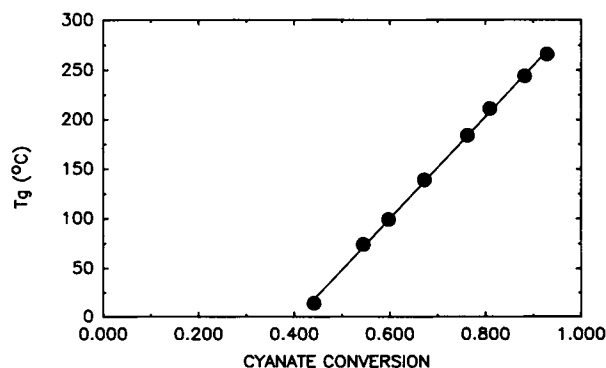


Figure 7 Glass transition temperature dependence on cyanate conversion for bisphenol A dicyanate resin.

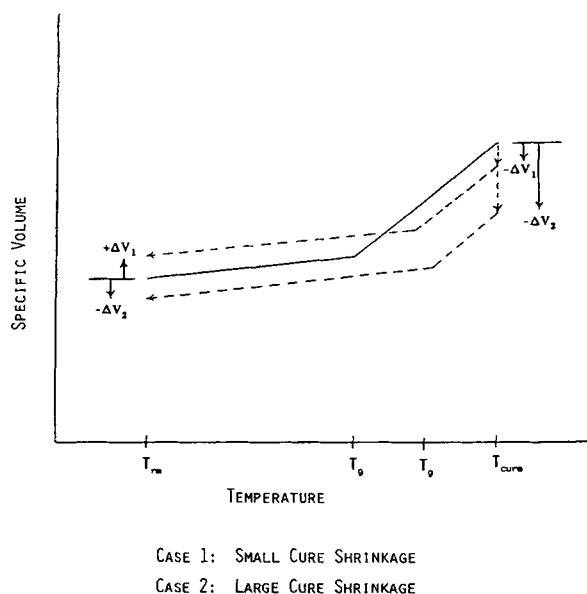


Figure 8 Sketch indicating how cure advancement with consequent glass transition temperature increase (T_g to T_g') may cause specific volume change in opposite directions (case 1) depending on the temperature of measurement (room temperature vs. cure temperature).

Propagation of Errors

The propagation of errors equation is obtained by taking the total differential of eq. (1) considering W_p , h , W_{Hg} , and T to be variables.

$$\begin{aligned}
 dV_{sp} = & \left\{ (1/W_p)c(1 + \beta_{py}(T - 25)) \right\} dh \\
 & - \left\{ (1/W_p)V_{sp,Hg}(1 + \beta_{Hg}T) \right\} dW_{Hg} \\
 & - \left\{ (1/W_p^2)[(ch + V_B)(1 + \beta_{py}(T - 25)) \right. \\
 & \left. + c(\Delta h)(\beta_{Hg} - \beta_{py})(\Delta T) \right. \\
 & \left. - W_{Hg}(V_{sp,Hg}(1 + \beta_{Hg}T)) \right\} dW_p \\
 & + \left\{ (1/W_p)[(ch + V_B)\beta_{py} \right. \\
 & \left. - W_{Hg}V_{sp,Hg}\beta_{Hg}] \right\} dT \quad (4)
 \end{aligned}$$

Equation (4) has the utility of assigning error contributions to each of these source variables. By assigning reasonable experimental numbers to the variables and conservative estimates for the accuracy in the differential terms (W_p , ≈ 1.0 g; c , ≈ 0.0087 mL/cm; T , $\approx 200^\circ\text{C}$; h , ≈ 20 cm; W_{Hg} , ≈ 25 g; V_B , ≈ 2.5 mL; dh , ≈ 0.05 cm; dW_p , ≈ 0.0005 g; dW_{Hg} , ≈ 0.001 g; dT , $\approx 2^\circ\text{C}$), the magnitude of these error contributions can be calculated. Inserting these values into eq. (4) yields the follow-

ing calculated result. The corresponding source variable derivative terms from eq. (4) are listed in the parenthesis below. No single variable dominates the error in the measurement.

$$\begin{aligned}
 dV_{sp} = & 0.00043 - 0.00008 - 0.00039 - 0.00062 \\
 & (dh) \quad (dW_{Hg}) \quad (dW_p) \quad (dT)
 \end{aligned}$$

Repetitive Measurements

A series of eight repetitive measurements were made on a partially cured bisphenol A dicyanate resin plug by two operators employing the same dilatometer apparatus and procedure. The dilatometer was dismantled and cleaned between each measurement. The eight specific volume measurements (0.8072, 0.8085, 0.8106, 0.8110, 0.8094, 0.8081, 0.8103, 0.8077 mL/g) have an arithmetic mean of 0.8091 mL/g and a standard deviation of 0.0013 mL/g.

The standard deviation is more than twice as large than would be anticipated from the propagation of errors. Two other sources of error may be considered; vacuum quality during mercury filling and joint grease seepage.

Considering vacuum quality, with the mechanical pump currently in use, it can range from 0.005 mm as a good vacuum to 0.025 mm as a poor vacuum. It is possible to calculate what the corresponding differential quantity of air might contribute to the measurement using approximate values of 3 mL for the dilatometer volume and 800 mm (1 atm + 40 cm mercury in capillary) for the dilatometer pressure.

$$\text{poor vacuum } V_{\text{air}} = (0.025/800)3.0 = 0.00009 \text{ mL}$$

$$\text{good vacuum } V_{\text{air}} = (0.005/800)3.0 = 0.00002 \text{ mL}$$

Thus, the vacuum quality is too small to be a factor in the measurement variation.

The vacuum grease on the bulb joint may be the factor. The extremes in the measurement are separated by 0.0038 mL. With a density close to 1, this represents 3.8 mg of grease. Any grease squeezed inside the effective dilatometer volume will have the effect of contributing to the polymer volume but not to the mass. The error then becomes proportional to the volume ratio of grease seepage to resin. As discussed in Section II, the grease application is a manual process subject to variation.

Authors acknowledge Office of Naval Research as sponsor for this investigation.

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Received August 2, 1993

Accepted September 28, 1993