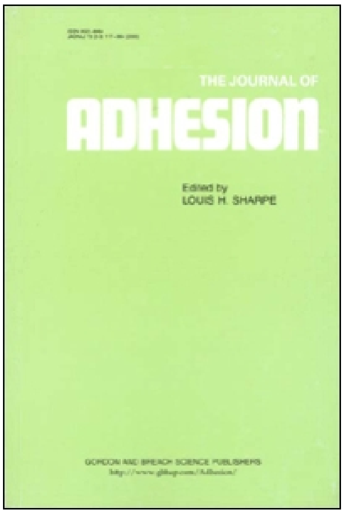

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DILATOMETRIC STUDY OF THE EFFECTS OF CURE PROFILES, FILLERS, AND MOLD CONSTRAINTS IN A MODEL EPOXY

Sandra L. Case[a]; Thomas C. Ward[a]
[a] Department of Chemistry, Blacksburg, VA, USA

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DILATOMETRIC STUDY OF THE EFFECTS OF CURE PROFILES, FILLERS, AND MOLD CONSTRAINTS IN A MODEL EPOXY

Sandra L. Case
Thomas C. Ward
Department of Chemistry, Virginia Polytechnic Institute and
State University, Blacksburg, VA, USA

A linear dilatometer was used to investigate the effects of cure conditions, mold types, and the presence of filler in a model epoxy. These studies revealed shrinkage in the cured epoxy when heating it through the glass transition region. The magnitude of the shrinkage, related to stress buildup in the epoxy during cure, was influenced by the epoxy processing conditions, filler content, and the nature of the mold used to contain the resin. Curing at a lower temperature, prior to a post-cure, decreased the magnitude of observed shrinkage. Annealing samples outside the mold allowed stresses that developed during the cure process to be reduced and led to less shrinkage observed than for samples annealed in the mold. Samples cured in a silicone mold exhibit less shrinkage in the dilatometer than samples cured in an aluminum mold. Soaking samples in water prior to dilatometric analysis led to stress relaxation in the sample and decreased the observed shrinkage. Specimens containing titanium dioxide filler exhibited less shrinkage than unfilled samples. The filled samples also exhibited less expansion slightly above the glass transition temperature. The reduced expansion might arise from restricted chain mobility in the presence of the filler.

Keywords: Dilatometer; Shrinkage; Stress; Cure condition; Mold constraint; Filler

INTRODUCTION

Factors such as temperature change, absorption of fluids, applied mechanical stresses, and chemical reactions can lead to dimensional

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Present address of Sandra Case is: Lord Corporation, Thomas Lord Research Center, Cary, NC, USA.

Address correspondence to Thomas C. Ward, Virginia Tech, Department of Chemistry, 2107 Halm Hall (0344), Blacksburg, VA 24061, USA. E-mail: tward@vt.edu

changes in polymers. Using a dilatometer, the dimensional changes of a sample can be monitored. The typical behavior of the specific volume of a glassy polymer in response to temperature is shown in Figure 1. As the polymer is heated, the volume increases linearly with temperature, with a change in slope at the glass transition temperature (T_g). In our studies, an anomaly was observed in the dilatometric behavior at T_g. This article addresses some possible causes of the anomalous results.

In many adhesive applications, epoxies are geometrically constrained during cure, leading to residual stresses. These residual stresses are undesirable because they may lead to premature debonding of the epoxy from a substrate. Volume changes that occur in an epoxy during the cross-linking process are known to produce curing stresses [1, 2]. Optimizing the cure temperature–time profile of the epoxy may minimize stress formation [3]. Slower heating rates allow more time for the polymer to relax and relieve stresses created during cure [4]. In the present work, the influence of cure conditions, mold constraints, and filler content have been examined

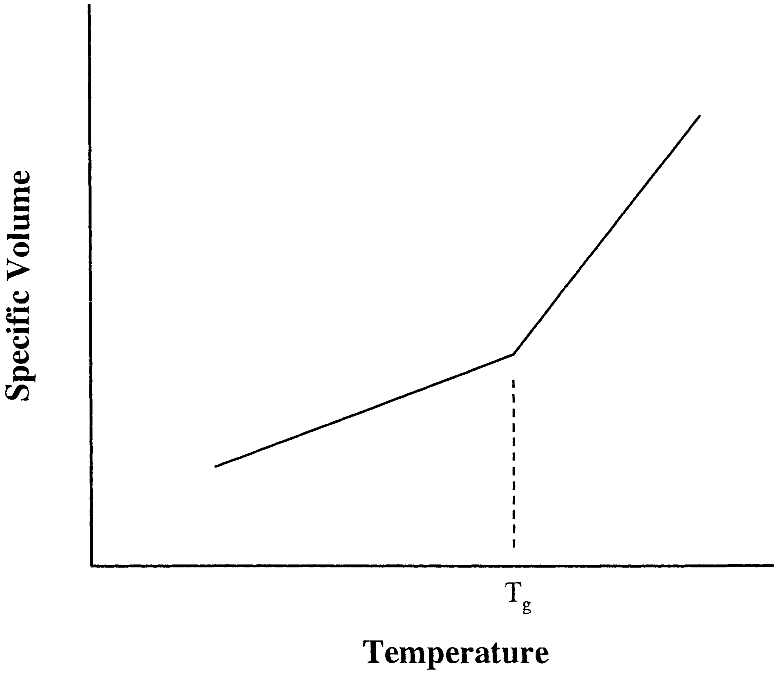

FIGURE 1 Specific volume *versus* temperature.

in order to understand their role in stress development in a model epoxy.

Fillers may be added to epoxies to increase the modulus, lower the thermal coefficient of expansion (CTE), and toughen the material. The addition of fillers can also affect epoxy properties by forming chemical and physical bonds on the surface of the filler, thereby changing the curing mechanism and leading to differences in cross-link density [5]. Incorporation of fillers can also lead to the formation of compressive stresses in the epoxy in the vicinity of the filler and tensile stresses in the matrix due to the differences in thermal expansion of the filler and epoxy [6–8]. In our investigation, we have examined the effect of the addition of titanium dioxide on the physical properties of our model epoxy using both dynamic mechanical analysis and dilatometry.

EXPERIMENTAL

Model Epoxy Components

Epon 862®, a bisphenol-F resin (shown in Figure 2a), was obtained from Shell Chemical Corporation (Houston, TX, USA). This resin has an epoxide equivalent weight of 171 g/mole. Titanium dioxide was purchased from Fisher Chemical (Pittsburgh, PA, USA) and, if used, was placed in the epoxy at concentrations of 10 and 20 parts per hundred resin (phr). The epoxy curing agent was 4-methyl-2-phenylimidazole (95% pure, Aldrich Chemical, St. Louis, MO, USA). The structure is shown in Figure 2b. In imidazole cures, the reaction

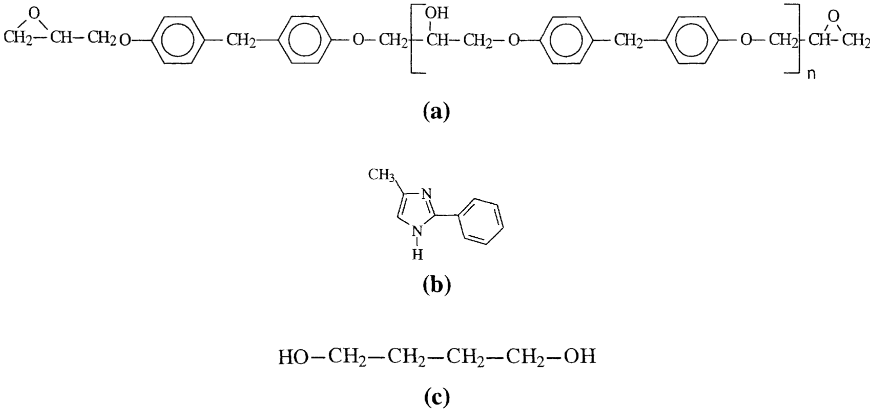

FIGURE 2 Model epoxy components: (a) Epon 862® (bisphenol-F epoxy), (b) 4-Methyl-2-phenylimidazole, and (c) 1,4-Butanediol.

mechanism involves addition it to the epoxy ring to form an imidazole-epoxy complex. The hydroxy adduct then initiates the epoxy ring opening, which leads to chain propagation [9, 10]. Three phr of the imidazole was added to cure the epoxy [11]. Ten phr of 1,4-butanediol purchased from Aldrich (Figure 2c) was incorporated into the model system. The 1,4-butanediol is thought to toughen the otherwise brittle epoxy through chain transfer by either (1) increasing the number of chain ends if one of the hydroxyl groups reacts or, (2) chain extension when both hydroxyl groups react. Both cases lead to a cross-linked network with a lower glass transition temperature and improved flexibility.

Sample Preparation

Epoxy resin (10–15 g) and 1,4-butanediol (10 phr), were placed in a round-bottom flask and heated to 75°C with an oil bath. The 4-methyl-2-phenylimidazole (3 phr) was then added to the round-bottom flask and the materials were mechanically stirred for 20 min at 75°C. Titanium dioxide, if used, was added last and stirred for an additional 10 min at the mixing temperature.

The epoxy was placed in molds to cure at various times and temperatures. In most cases, the samples were cured in aluminum molds with interior dimensions of $52\,\text{mm} \times 5\,\text{mm} \times 2\,\text{mm}$. The aluminum molds were coated with a fluorocarbon mold release agent and then baked in the oven at 250°C to remove excess release agent before adding the epoxy. For a few samples, the epoxy was also cured in a silicone mold (interior dimensions: $38\,\text{mm} \times 6.3\,\text{mm} \times 3.1\,\text{mm}$) fabricated from Dow Corning 3120 RTV silicone rubber (Midland, MI, USA). The silicone molds were partially filled to generate samples with the same thickness as those cured in the aluminum mold.

Thermal Analysis

Dilatometry, differential scanning calorimetry (DSC), and dynamic mechanical analysis (DMA) were employed to measure thermal properties of the epoxy. For each experimental condition, three samples were tested. The average and one standard deviation of the three samples are reported.

Length changes of the epoxy as a function of temperature were measured using a Netzsch Dilatometer 402 C (Burlington, MA, USA). A 0.30 N force was applied, and the epoxy samples were heated at 2° C/min under a nitrogen purge. The samples were approximately

5 mm wide and 2 mm thick. The sample length varied between 15 and 18 mm.

DSC was completed using a Dupont Instruments® DSC 912 (New Castle, DE, USA). Samples (~10 mg) were measured at 10°C/min under a 30 ml/min nitrogen purge in Seiko® (Shelton, CT, USA) hermetically sealed pans.

Dynamic mechanical response was determined on a Netzsch DMA 242 (Burlington, MA, USA). Measurements were taken in the dual cantilever mode using a frequency of 1 Hz. An oscillation amplitude of 7.5 μm was employed. The sample geometry was approximately 52 mm × 5 mm × 2 mm.

Experimental Conditions

- The influence of different cure conditions on dilatometric behavior was studied by investigating five different cure profiles:

1. 130°C (1 h)
2. 80°C (2 h), 180°C (2 h postcure)
3. 130°C (1 h), 180°C (2 h postcure)
4. 80°C (1 h), no postcure
5. 80°C (2 h), no postcure

For the various cure profiles, the epoxy was dispensed in a mold and placed in an oven that had been preheated to the desired cure temperature for the specified time. For samples containing a postcure, the oven was immediately ramped to the desired postcure temperature following the initial cure step. On completion of the cure cycle, the molds were removed from the oven and allowed to cool under ambient conditions.

- Mold constraints on dilatometric behavior were investigated by performing second heats of samples in the mold also and freed from the mold. The samples had been cured at 130°C for 1 h prior to these annealing conditions.
- Mold constraints were also examined by noting differences in dilatometric properties of samples that had been cured in aluminum or silicone molds at 130°C for 1 h.
- Mold heating rate during cure on dilatometric behavior was investigated.
- Moisture absorption effects were studied by soaking samples in deionized water at 60°C for two weeks prior to testing in the dilatometer.

- The influence of filler content on dilatometric properties was examined by adding titanium dioxide to the epoxy prior to cure and curing at 130°C for 1 h.

RESULTS AND DISCUSSION

Effect of Cure Temperature and Cure Time

DSC was used to determine the difference in extent of cure for 1 h at 80°C *versus* 2 h at 80°C (with no postcure). Neither curing at 80°C for 1 h nor for 2 h fully cured the model sample, and an exothermic peak was observed in subsequent DSC isotherms. The areas of the exothermic peaks are shown in Table 1. Comparison of this exothermic peak area to the exothermic peak area of a sample with no cure can be used to determine the extent of reaction of the material using the following relationship:

$$x = 1 - \frac{\Delta H_t}{\Delta H_0}, \tag{1}$$

where ΔH_t is the residual heat evolved for a partially cured material, ΔH_0 is the total heat of reaction evolved for the sample with no cure, and x is the degree of conversion. The DSC analysis results are also shown in Table 1. After 1 h at 80°C, the sample is 91% cured. After 2 h at 80°C, the sample is 95% cured.

These partially cured samples were examined in a linear dilatometer. The average change in length normalized by the initial length is plotted as a function of temperature for each processing condition and is shown in Figure 3. The samples exhibit shrinkage on heating through the glass transition temperature. The calculated shrinkage is shown in Table 2. Epoxies cured at 80°C for 2 h exhibit less shrinkage than those cured at 80°C for 1 h. It is known that epoxies contract during cure. This results in greater shrinkage observed in the sample cured for only 1 h because it is undergoing further cure during the temperature rise in the dilatometer.

TABLE 1 DSC Residual Heats of Reaction

Sample	ΔH (J/g)	% Cure
No cure	308.6 ± 2.4	0
80°C 1 h	27.2 ± 2.0	91 ± 0.6
80°C 2 h	15.1 ± 1.6	95 ± 0.5

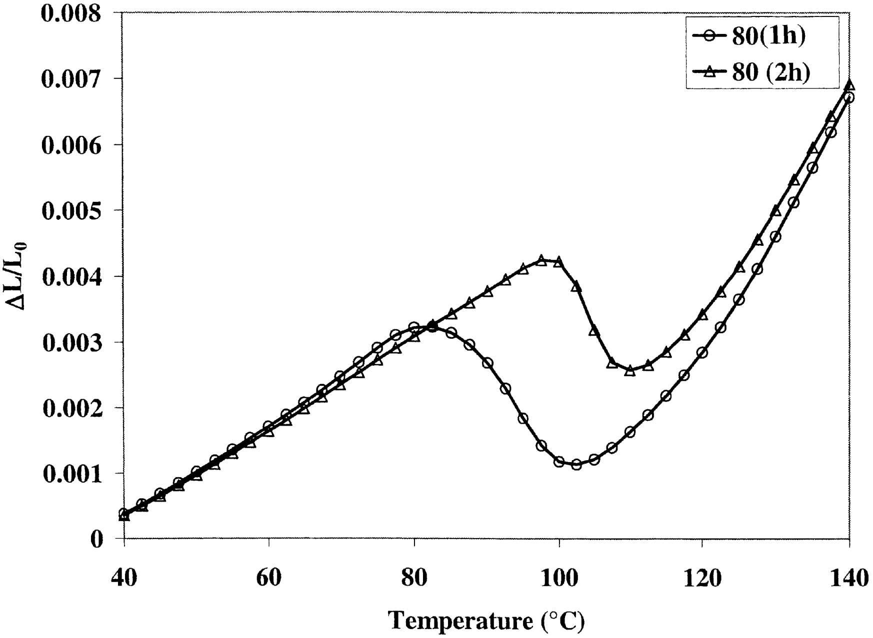

FIGURE 3 Dilatometry results for samples cured at 80°C for 1 or 2 h.

Coefficients of thermal expansion (CTE) were calculated from the dilatometry data using:

$$\alpha_l(T) = \frac{1}{l_0}\left(\frac{\partial l}{\partial T}\right)_p, \tag{2}$$

where α_l is the length expansion coefficient and l_0 is the initial length. CTEs were calculated in the region below the glass transition temperature (α_g) and in the rubbery state above the glass transition temperature (α_τ). The results are shown in Table 2. No differences were observed in the CTEs for the samples with different extents of cure either above or below the glass transition temperature.

TABLE 2 Influence of Cure on Dilatometry Results—Undercured Samples

Sample	$(\Delta L/L_0) * 1000$	α_g (ppm/°C)	α_r (ppm/°C)
80°C (1 h)	2.16 ± 0.65	70 ± 1	196 ± 2
80°C (2 h)	1.68 ± 0.3	66 ± 9	175 ± 22

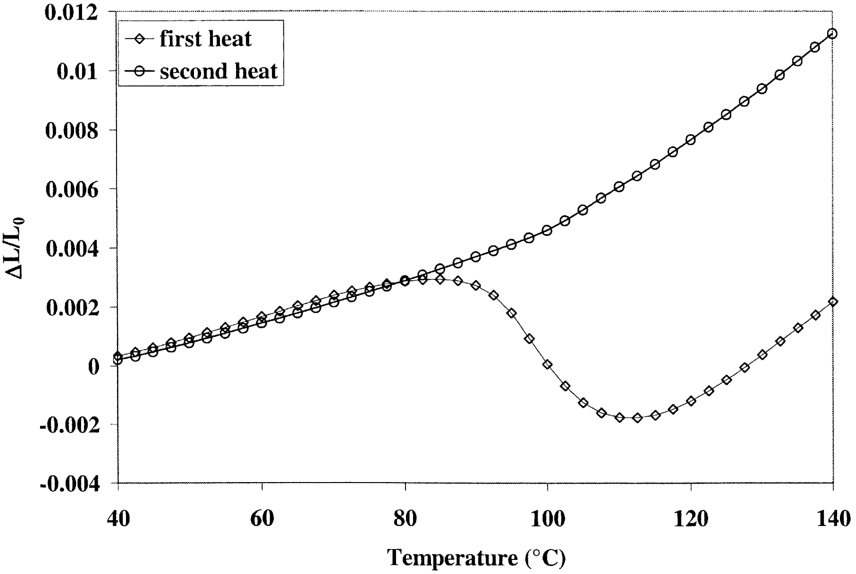

FIGURE 4 Dilatometry results for samples cured at 130°C for 1 h, first and second heats.

The analysis above contains no surprises and indicates that shrinkage in the dilatometer may result from incomplete cure of the samples. However, a sample cured at 130°C for 1 h was also examined. DSC analysis indicated this sample to be fully cured. In this case, shrinkage was still observed on heating the sample through the glass transition temperature in the instrument, as shown in Figure 4. To eliminate the possibility that the shrinkage was the result of the dilatometer probe penetration in the sample, the sample was cooled in the dilatometer and a second cycle was performed. In the second test, no shrinkage occurred and typical CTE discontinuity behavior was observed at the glass transition temperature, indicating that the shrinkage in the first heat was not the result of probe penetration in the sample. CTEs were also calculated and are shown in Table 3; no differences were observed for the first and second heat.

To examine further the cause of the shrinkage during the first heating experiment of our epoxy, two other full cure (as determined by DSC) profiles were also examined, and the results are shown in Figure 5. Again, unlike the typical dilatometric response shown in Figure 1, these samples shrink as the epoxy passes through the glass transition temperature. The calculated magnitude of shrinkage is shown in Table 4 and ranges up to over 0.5% (linear). Curing more

TABLE 3 Dilatometry Results for the Model Epoxy Cured at 130°C for 1 h

Sample	α_g (ppm/°C)	α_r (ppm/°C)
First heat	69 ± 3	178 ± 9
Second heat	68 ± 6	178 ± 12

slowly (80°C, 2 h/180°C, 2 h), leads to less shrinkage observed in the dilatometer than curing more rapidly (130°C, 1 h).

In order to ensure that it was the slower initial cure step, and not the postcure step, that led to less shrinkage, samples were also cured at 130°C for 1 h followed by the same 180°C postcure for 2 h. Within the error, the results for this sample are identical to samples with a 130°C, 1 h cure with no postcure. Thus, it was the slower initial cure step, and not the postcure step, that led to the observed differences in the samples.

Curing at lower initial temperatures for longer times results in less stress in the sample. On heating in the dilatometer, the polymer chains acquire excess free volume and mobility in the vicinity of the glass transition temperature. Then, as the polymer chains relax,

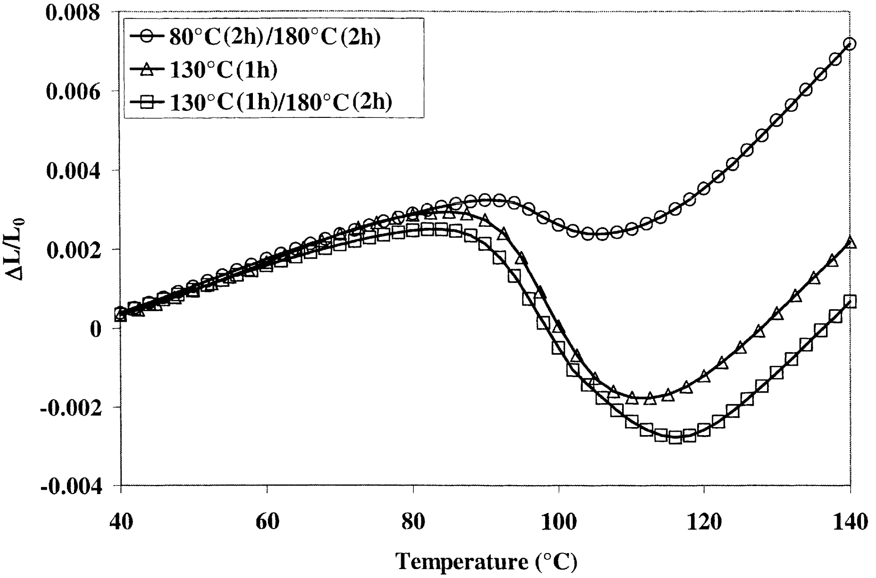

FIGURE 5 Dilatometry results for the model epoxy with different cure profiles.

TABLE 4 Influence of Cure on Dilatometry Results—Fully Cured Samples

Sample	$(\Delta L/L_0) * 1000$	α_g(ppm/°C)	α_r(ppm/°C)
130°C (1 h)	4.71 ± 0.30	69 ± 3	178 ± 9
130°C (1 h)/180°C (2 h)	5.45 ± 1.37	59 ± 5	175 ± 16
80°C (2 h)/180°C (2 h)	0.85 ± 0.35	67 ± 4	190 ± 9

stresses that were created during cure are released, leading to the observed shrinkage. Therefore, less stress generated during cure leads to less shrinkage observed in the dilatometer when the sample is reheated through the glass transition temperature. These differences in shrinkage due to stresses developing during cure are consistent with the results of Prasatya *et al.* [2], who demonstrated that cure history plays an important role in the magnitude of residual stress present after cure. Their results suggest that residual stresses are minimized in a two-step cure in which the initial temperature is much smaller than the postcure temperature.

Effect of Cure in Molds

Influence of Second Heat in or out of Mold

It was postulated that the mold surfaces were constraining the samples during polymerization, thus causing the stress buildup and later shrinkage of the epoxy in the dilatometer; other work in the literature has demonstrated that in volumetrically constrained epoxies large stresses develop due to cure shrinkage and thermal expansion/contraction [12]. Therefore, the effects of mold constraints on stress relief were studied by heating the epoxy samples after cure (130°C for 1 h) above the glass transition temperature either (1) in the mold or (2) free of the mold. The dilatometry results are shown in Figure 6 and the calculated shrinkage is displayed in Table 5. Heating samples out of the mold allowed stresses that developed during the curing to be reduced, leading to less shrinkage observed in the dilatometer. However, samples reheated in the mold were constrained and stresses generated during cure could not be relieved; therefore, greater shrinkage was observed in the dilatometer. No differences were observed in the CTEs in either case.

Influence of Mold Type: Silicone Mold versus Aluminum Mold

To examine further the effects of mold constraints, specimens were cured in a silicone mold and compared with otherwise identical ones

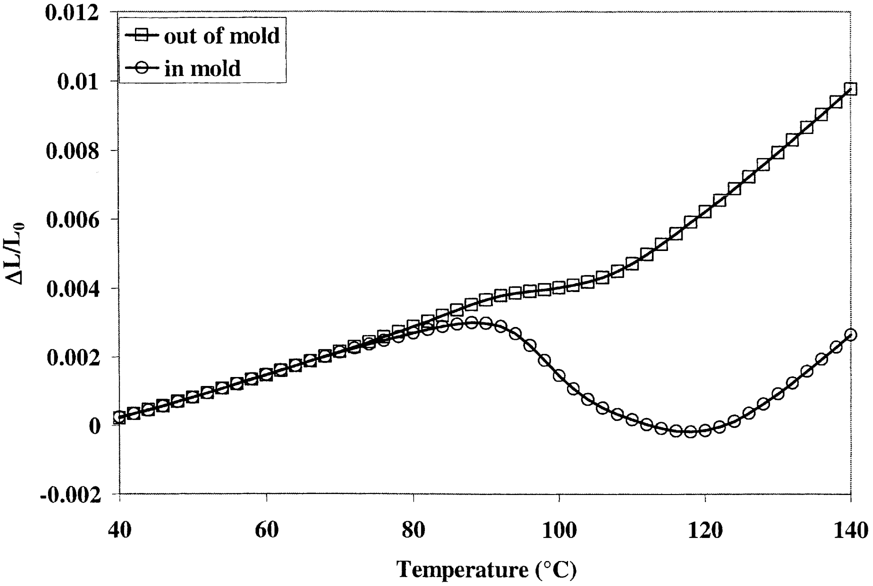

FIGURE 6 Dilatometry results for the model epoxy annealed in or out of the mold after curing at 130°C for 1 h.

cured in an aluminum mold. Samples were cured at 130°C for 1 h. These outcomes are shown in Figure 7 and Table 6. We note that specimens cured in the silicone mold exhibit less shrinkage on heating than those cured in the aluminum mold. Some of the reasons for this effect could be as follows: (1) the surface energy of the silicone is lower, and thus the poorly adhering epoxy is not constrained as it contracts on polymerization; (2) the silicone is more compliant than the epoxy, thus allowing stress relief; and (3) the CTE mismatch is greater for aluminum and epoxy than for silicone and epoxy. All of these factors would lead to greater constraints and higher stresses in the epoxy when the aluminum mold was utilized, thus creating more measured shrinkage in the dilatometer. These results are consistent with Kan *et al.* [13],

TABLE 5 Influence of Mold Constraints During Annealing on Dilaatometry Results

Sample	$(\Delta L/L_0) * 1000$	α_g (ppm/°C)	α_r (ppm/°C)
Annealed in mold	3.41 ± 0.8	64 ± 3	160 ± 14
Annealed out of mold	0.04 ± 0.04	65 ± 9	181 ± 4

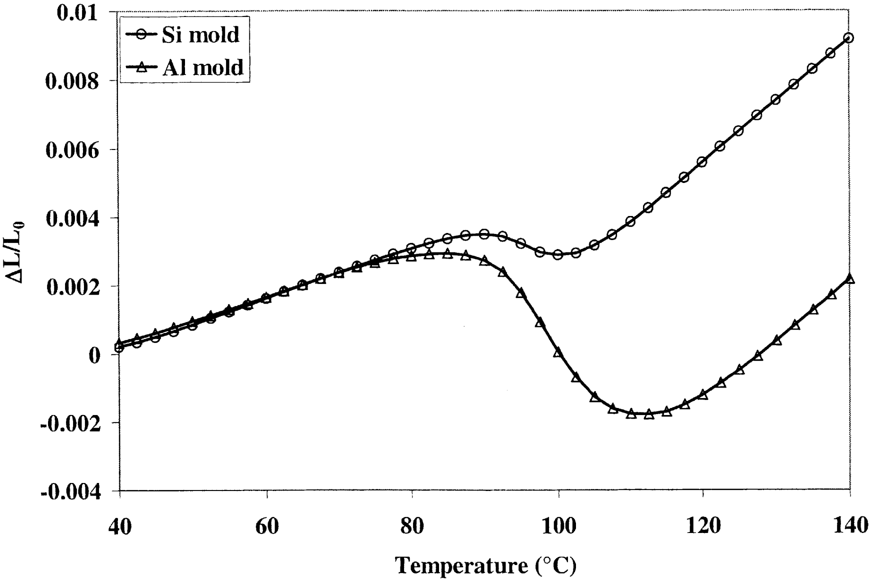

FIGURE 7 Dilatometry results for samples cured in silicone *versus* aluminum molds at 130°C for 1 h.

who have also indicated anomalous dilatometric curves as a result of stresses introduced during processing due to adhesion of the polymer to the side of the mold. Within experimental error, no differences were observed for the various CTEs of these experiments.

Effect of Cure Heating Rate

Since silicone, rubber, and aluminum have large differences in heat capacity, it was of interest to ensure that the mold effects discussed above were not due to unforeseen heating rate differences in the curing profiles. A thermocouple was placed in each of two molds, which were in turn set in an oven at 130°C. The temperature was recorded as a function of time, and the results are displayed in

TABLE 6 Influence of Mold Type on Dilatometry Results

Sample	$(\Delta L/L_0) * 1000$	α_g (ppm/°C)	α_r (ppm/°C)
Al mold	4.7 ± 0.3	69 ± 3	178 ± 12
Si mold	0.6 ± 0.3	74 ± 3	180 ± 3

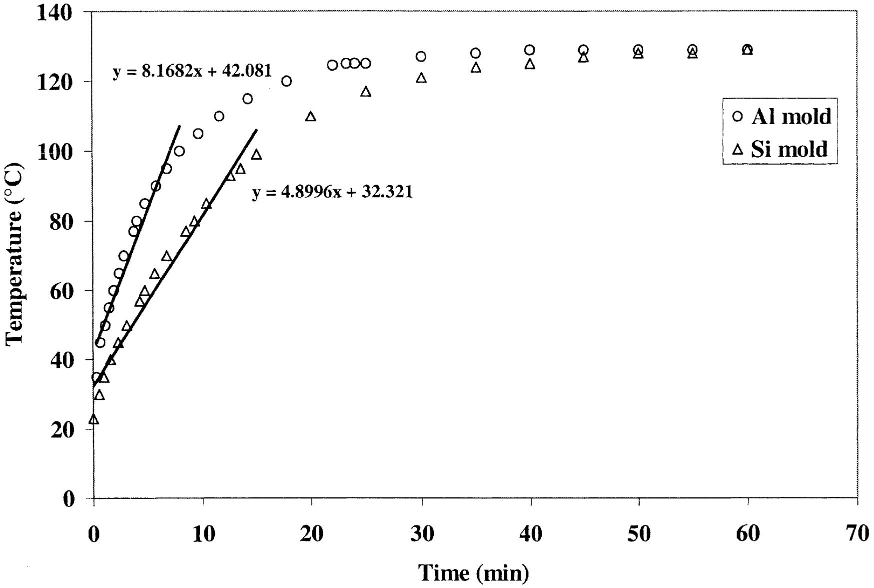

FIGURE 8 Temperature ramp profile for aluminum and silicone molds placed in an oven preheated to 130°C.

Figure 8. The silicone mold heats at a slightly slower rate than the aluminum mold under these conditions. The heating rate was calculated from room temperature to 100°C—the initial heating rate was approximately 8°C/min and 5°C/min for the aluminum and silicone molds, respectively. Thus, to isolate the effect of heating rate on shrinkage, specimens that were placed in an oven preheated to 130°C and cured for 1 h were compared with samples placed in the oven at room temperature and cured by heating at 2°C/min to 130°C followed by holding at 130°C for 1 h. Using this temperature–time profile, the aluminum mold heats at approximately the same rate as the oven (2°C/min), as shown in Figure 9. The dilatometry results for curing at these different heating rates are shown in Figure 10 and Table 7. The important conclusion is that the heating rate does influence the magnitude of shrinkage, with curing at slower rates leading to less shrinkage, which is in line with the results of Plepys and Farris [14] who demonstrated that a temperature ramp cure resulted in lower residual stress relative to an isothermal cure. It is equally important that the measured difference is not large enough to be the sole cause of the lower shrinkage observed in the samples cured in the silicone mold when compared with the aluminum mold. In

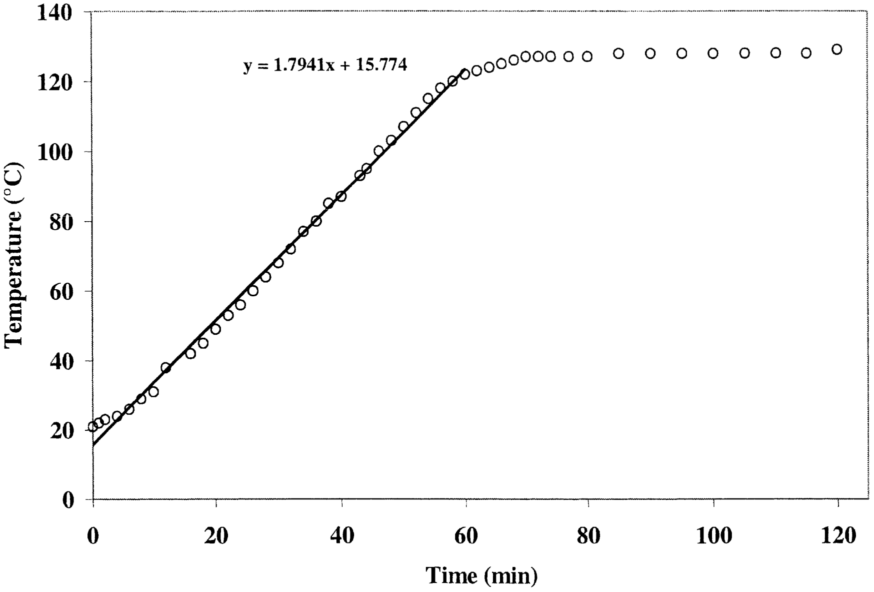

FIGURE 9 Temperature ramp profile for an aluminum mold placed in the oven at RT and heated to 130°C at 2°C/min.

other words, both factors play a role in residual stress developed during cure. Again, no differences were observed in the CTEs.

Influence of Moisture Soaking

The influence of aging the model epoxy in water on dilatometric behavior was also examined. Samples were cured at 130°C for 1 h and then placed in deionized water at 60°C for two weeks. Soaking the samples in water under these conditions resulted in a moisture uptake of $2.7 \pm 0.1\%$. The aged samples were examined in the dilatometer, as described above, recognizing, that some water loss would occur at the elevated temperature, and the results are displayed in Figure 11 and Table 8. Moisture absorption plasticized the epoxy and lowered its glass transition temperature (interpreted as the inflection point of the shrinkage curve) from 99°C to 75°C. The moisture uptake also led to a residual stress relaxation in the material. Therefore, less shrinkage was observed in the dilatometer compared with unsoaked materials. Thus, the reduction of the stresses by exposing the material to moisture led to a decrease in the observed

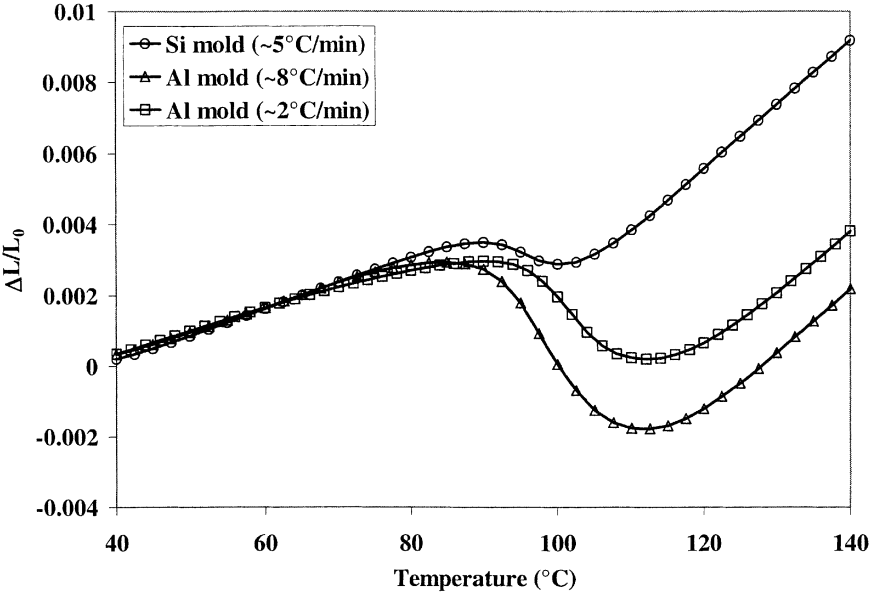

FIGURE 10 Dilatometry results for samples cured at different initial heating rates.

shrinkage in the dilatometer, which further demonstrates that the anomalous observed shrinkage is a result of stresses present in the epoxy. A second heating step was performed on the samples. We found the glass transition temperature in the second heat to be the same as that for an untreated dry sample, indicating that most of the water was removed during the first heating step. Since stresses were relieved during soaking and also by the first heat, minimal shrinkage is observed in the second heat.

CTEs were calculated for the cured epoxies that had been aged in water and are shown in Table 8. No changes were observed in the CTEs in the glassy region. However, the CTE in the rubbery region

TABLE 7 Influence of Heating Rate During Cure on dilatometry Results

Sample	$(\Delta L/L_0) * 1000$	α_g (ppm/°C)	α_r (ppm/°C)
Si (~5°C/min)	0.6 ± 0.3	74 ± 3	180 ± 3
Al (~8°C/min)	4.7 ± 0.3	69 ± 3	178 ± 12
Al (~2°C/min)	2.7 ± 0.9	64 ± 6	166 ± 10

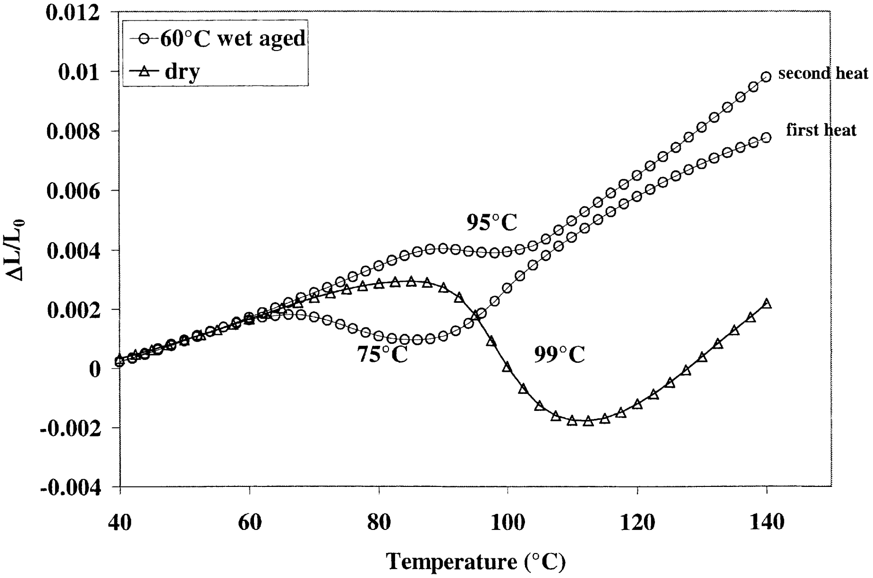

FIGURE 11 Dilatometry results for the model epoxy after aging in moisture two weeks at 60°C.

from the first heat cycle of the wet sample is lower than that of a dry sample. In the rubbery region, water is clearly desorbing from the sample. This results in a decrease in the overall sample dimensions, causing a decrease in the observed CTE. It is not known if this deswelling shrinkage is isotropic. In the second heat, the CTE in the rubbery region of the soaked epoxies is the same, within our error, as the dry samples, indicating that the majority of the water was removed during the first heat in the dilatometer.

Filler Content

Titanium dioxide particles were added to the model epoxy. The fillers were examined with XPS prior to adding them to the epoxy. The atomic

TABLE 8 Dilatometry Results after Soaking in Water at 60°C

Sample	$(\Delta L/L_0) * 1000$	T_g (°C)	α_g (ppm/°C)	α_r (ppm/°C)
Dry	4.7 ± 0.3	99 ± 3	69 ± 3	178 ± 12
Wet first heat	0.88 ± 0.03	75 ± 3	72 ± 6	124 ± 6
Wet second heat	0.13 ± 0.09	95 ± 2	75 ± 3	161 ± 15

TABLE 9 XPS Atomic Concentration of TiO_2

Element	% Atomic concentration
C	21.8
O	56.6
Ti	21.6
Zr	nd
Al	nd
Si	nd
N	nd

nd not detected (< 0.2%).

concentration results for the filler are shown in Table 9. The analysis indicates that the titanium dioxide contains no surface treatment, as evidenced by the presence of only titanium, oxygen, and carbon.

SEM was used to examine the particle size of the filler. The micrograph is shown in Figure 12. The particles are approximately 20–25 μ in diameter. The tan deltas as a function of temperature (from DMA) for the model epoxy having no filler with 10 phr of titanium dioxide and with 20 phr of titanium dioxide are shown in Figure 13. The glass transition temperature (from tan delta peak), tan delta height, and

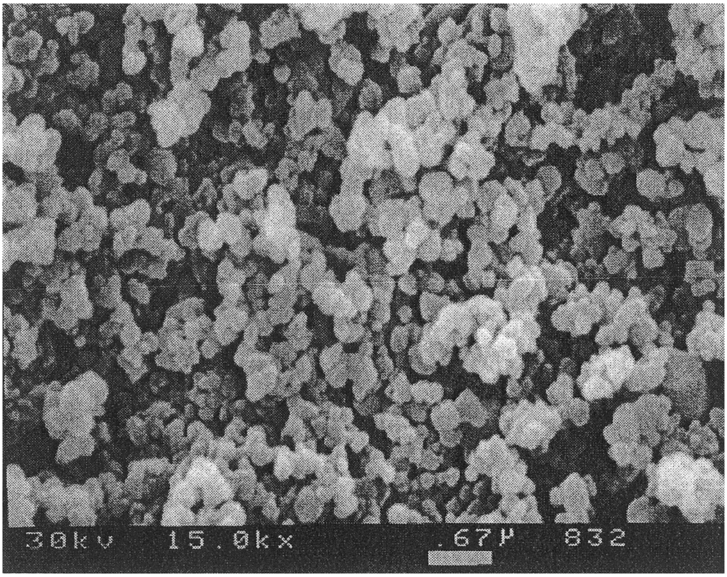

FIGURE 12 SEM of titanium dioxide.

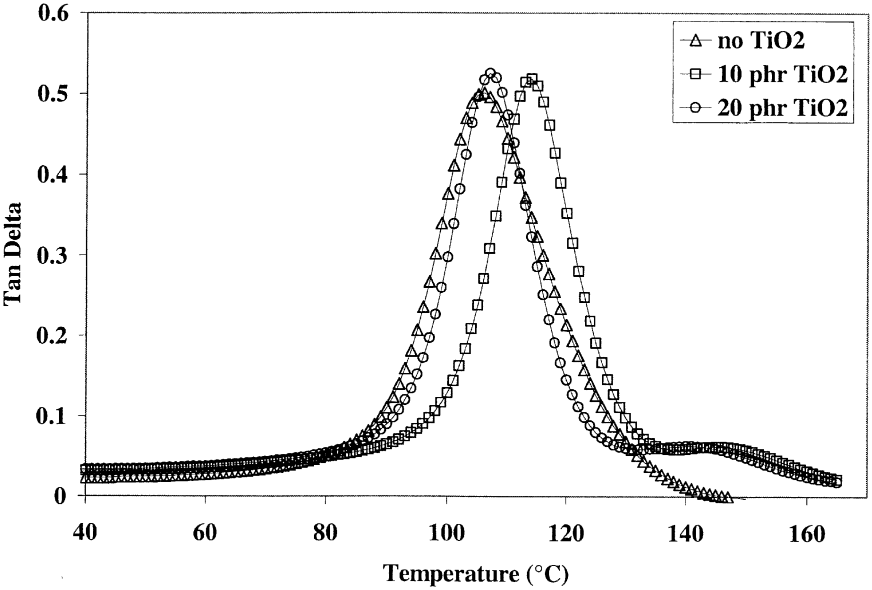

FIGURE 13 DMA results (1 Hz) for the model epoxy containing titanium dioxide cured at 130°C for 1 h.

width-at-half-height are listed in Table 10. The sample with 10 phr of titanium dioxide exhibits the highest glass transition temperature. However, there is a reversal of the anticipated trend of filler effects as the more highly loaded epoxy, with 20 phr of titanium dioxide shows a tan delta temperature signature only slightly shifted from that of the neat epoxy. There is a large body of literature on filler effects on epoxy performance. Briefly, we note that other authors have reported an increase in the glass transition temperature upon addition of fillers to epoxies [5, 15–17]. The increase in the glass transition temperature is speculated to be the result of constraining the polymer chains in the presence of the filler. However, in our case, addition of 20 phr titanium dioxide did not affect the glass transition temperature, so multiple

TABLE 10 DMA Results for the Model Epoxy Containing titanium Dioxide

Sample	*Tg* (°C)	Tan delta height	Width-at-half-height (°C)
0 phr	105.5 ± 1.3	0.55 ± 0.06	22 ± 2
10 phr	113.8 ± 0.5	0.52 ± 0.01	17 ± 1
20 phr	107.1 ± 0.1	0.52 ± 0.01	15 ± 1

events are implicated. The larger amount of filler may lead to lower conversions and thereby lower the cross-link density of the epoxy, yet the filler may still constrain the polymer chains. These two opposing effects may give rise to a glass transition temperature similar to the sample with no titanium dioxide and an even lower glass transition temperature than the sample with 10 phr of titanium dioxide.

Within the experimental error, the height of the tan delta peak was not affected by the addition of the filler. However, both filled samples exhibit a small peak just above the glass transition temperature (at approximately 140°C) that is not present in the unfilled samples. Tsagaropoulos and Eisenberg [18] observed similar behavior for several polymers filled with silica particles. They and others attribute the second peak, or shoulder, to reduced mobility of the polymer chains bound to the filler.

Two Gaussian curves were fit to the tan delta peak data to determine the width at half height of the main relaxation. The peak width decreased in the samples containing the titanium dioxide filler. A decrease in the width of tan delta indicates a more homogenous molecular environment contributing to the cooperative motions required for a glassy dispersion of energy. The decrease in energy dissipation and the appearance of the second peak are interesting, suggesting strong interfacial interactions between the filler and the epoxy and a restricted mobility of the epoxy in the presence of the filler, creating a "bimodal" set of relaxing volume elements [16, 18].

Dilatometry was also used to investigate the model epoxy filled with titanium dioxide. The results of the first heat of the neat model epoxy and the epoxy containing 10 and 20 phr of titanium dioxide are plotted in Figure 14. Again, the samples are found to shrink while passing through the glass transition temperature. It can be seen from Figure 14 that the thermal response is consistent with the DMA conclusions above. If we regard the initial "knee" in the dilatometric expansion/shrinkage plots as the glass transition temperature, then the result for the epoxy with 20 phr filler falls between that of the unfilled and 10 phr filled samples. Furthermore, all the samples begin to shrink on passing the glass transition temperature, and then they expand at a much reduced rate between 105–120°C followed by a temperature region where more typical expansion is observed. Although the temperature range of the slow rate of expansion does not exactly correspond to the temperature of the second peak in tan delta, it is believed that the origin of the mechanisms is similar, with differences in effective test rate coming into play. Again, incorporation of the filler is postulated to reduce the mobility of the polymer chains and thus prevent dimensional changes until heating to higher temperatures.

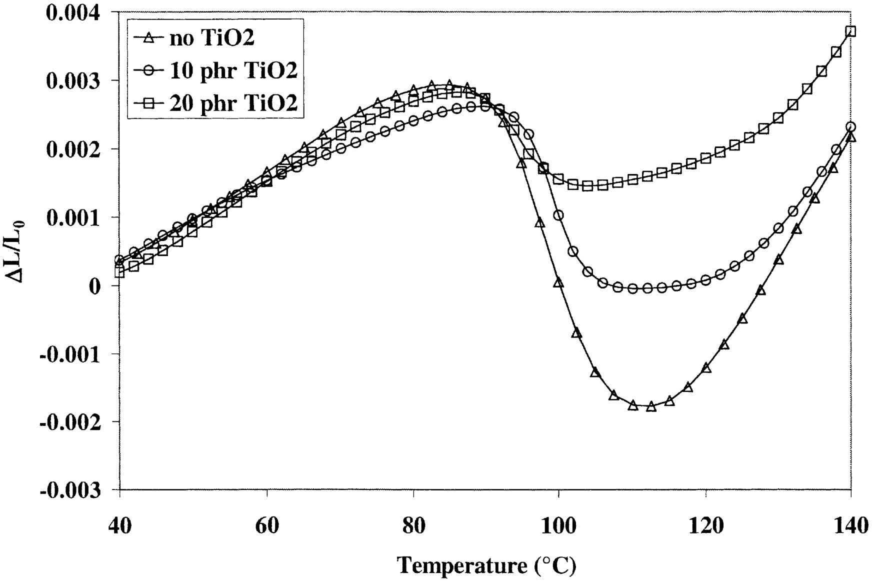

FIGURE 14 Dilatometry results: first heat of the model epoxy containing titanium dioxide cured at 130°C for 1 h.

A second heat was conducted on these filled epoxies in the dilatometer, and the results are shown in Figure 15. The samples exhibit typical expansion behavior, and very little difference is observed among the different sample types. Clearly, a satisfactory model for the behavior of these filled epoxies containing residual stress is not available at this time, and further data is necessary.

Coefficients of thermal expansion were calculated below and above the glass transition temperature for the first and second heats and are shown in Tables 11 and 12 respectively. The sample containing 10 phr titanium dioxide has a lower glassy CTE than the 20 phr and neat samples in the first heat. This may be due to restricted mobility of the polymer chains bound to the filler particles. The lack of difference at 20 phr as compared with 10 phr may again arise from a lower crosslink density in the epoxy due to the filler inhibiting the cure. Incorporation of 10 and 20 phr filler led to lower rubbery CTEs than the unfilled specimen, indicating that the filler restricts the mobility of the polymer chains. Minor differences were observed in the CTEs in the glassy and especially the rubbery regions of the second heat step, indicating that the presence of the filler leads to structural differences in the epoxy that are minimized after heating above the glass transition temperature one time.

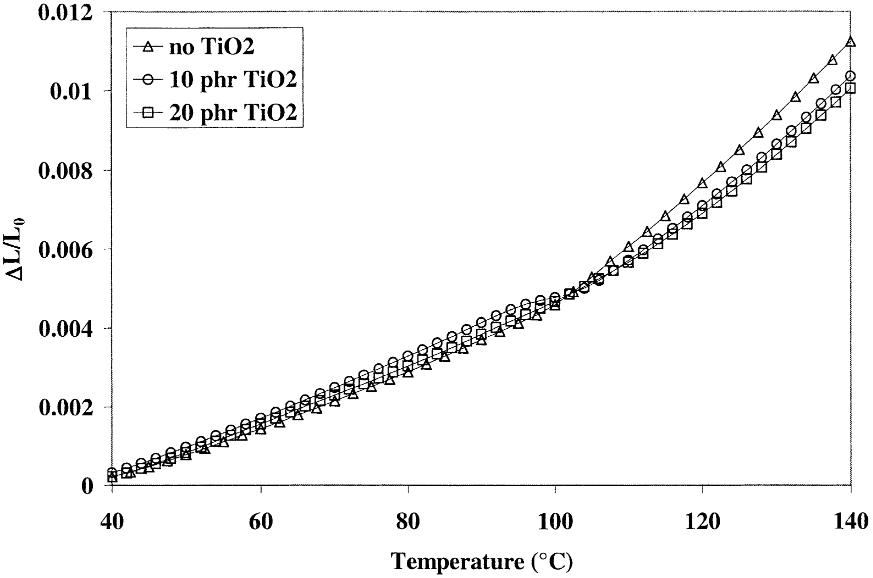

FIGURE 15 Dilatometry results: second heat of the model epoxy containing titanium dioxide cured at 130°C for 1 h.

CONCLUSIONS

The cure cycle of a model epoxy system was varied to investigate its influence on residual stresses using linear dilatometry. Fully cured samples were observed to shrink while being reheated through their glass transitions. The amount of shrinkage is synergistically dependent on the cure cycle and on constraints arising from the molds necessary to contain the specimens during curing. Advancing the cure at a lower temperature before a postcure step reduced the amount of subsequent shrinkage observed in the dilatometer by allowing more time for the polymer to relax, thus relieving cure stresses. Curing samples in a silicone mold led to less shrinkage detected by the dilatometer

TABLE 11 Dilatometry Results for the Model Epoxy Containing Titanium Dioxide—First Heat

Sample	$(\Delta L/L_0) * 1000$	α_g (ppm/°C)	α_r (ppm/°C)
0 phr	4.7 ± 0.3	69 ± 2	178 ± 12
10 phr	2.7 ± 0.3	55 ± 5	128 ± 14
20 phr	1.4 ± 1.4	70 ± 4	122 ± 23

TABLE 12 Dilatometry Results for the Model Epoxy Containing Titanium Dioxide—Second Heat

Sample	α_g (ppm/°C)	α_r (ppm/°C)
0 phr	68 ± 6	178 ± 12
10 phr	73 ± 2	168 ± 5
20 phr	71 ± 5	160 ± 7

than curing samples in an aluminum mold. In general, although there were some heating rate influences, the silicone rubber molds placed less constraints on the system during cure and generated more stress-free products. It is believed that if the epoxy could be cured without a mold, no shrinkage would be observed. Soaking samples in water leads to stress relaxation due to moisture sorption and, consequently, lower shrinkage.

Addition of titanium dioxide filler at two concentrations to the model epoxy produced an additional peak in the tan delta and a narrower width-at-half-height of tan delta. These changes may be due to strong interactions and a resulting reduced mobility of the epoxy chains in the presence of the filler. The reduction in mobility with the incorporation of the filler also led to changes in the CTEs of samples taken above the glass transition temperature for the first time, but not on a second heating step. It is indicated that the filler led to molecular-level structural differences in the epoxy that were removed after heating above the glass transition temperature, which is a complex process.

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