Evolution of residual stresses in three-dimensionally constrained epoxy resins

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Residual stresses arising from the curing process in a three-dimensionally constrained epoxy resin have been determined experimentally by a strain-gauge method. The results were analysed using the theory of incremental elasticity for an ageing, linear thermoelastic material subjected to dimensional constraints. It was found that large residual stresses developed in three-dimensionally constrained epoxy resins and that, by modifying the cure schedule, the internal stresses could be reduced. The bulk behaviour of the epoxy resin under volumetric constraints was also investigated. Values for the bulk modulus of the epoxy resin were calculated from the results at temperatures above and below the glass transition temperature of the resin.

INTRODUCTION

The processing of epoxy resins results in the formation of residual stresses within the material, which can greatly affect the performance of the finished product. The primary applications of epoxy resins include composites, coatings and adhesives. In all of these applications, the presence of residual stresses in the resin reduce its overall performance.

Owing to the importance of epoxy resins in structural applications, the subject of residual stresses in epoxy resins has received considerable attention in the literature. A number of investigators have studied residual stresses in epoxy resins used in simple geometries such as moulded bars or coatings[1-6]. In more complicated geometries, such as those found in a composite, the measurement is much more difficult. As a result, residual stresses have only been measured in simplified model composites[7,8]. For more intricate composites the residual stresses have been calculated by a number of investigators[9-13].

The magnitude of the residual stress developed in an epoxy resin is dependent on a number of factors. These factors include physical and mechanical properties such as the glass transition temperature, thermal expansion coefficients and elastic moduli of the epoxy resin. Other factors influencing the residual stress in the resin include the cure schedule used in processing the resin as well as the degree of dimensional constraint to which the resin is subjected. Previously, the methods used to measure residual stresses in epoxy resins involved constraining the resin in one or two dimensions. In composites, however, the degree of constraint within the resin can vary from one to three dimensions.

In the work presented here the residual stresses in three-dimensionally constrained epoxy resins are measured. Examination of the equations of incremental linear elasticity reveal that the internal stresses developed in a volumetrically constrained resin are the maximum

stresses that can occur in an epoxy resin due to the curing process. It is hoped that by understanding the formation of residual stresses in three-dimensionally constrained epoxy resins, methods can be developed to reduce residual stresses in composite materials.

THEORETICAL ANALYSIS

One way to get an idea of the magnitude of the residual stresses in an epoxy resin is to study the equations of linear elasticity. During the cure of an epoxy resin, however, the mechanical properties change dramatically. The resin goes from a liquid to a crosslinked rubber-like solid during the curing reaction and subsequently to a glassy material upon cooling below the glass transition temperature. The dramatic changes in material properties preclude the use of the general stress-strain equations of linear elasticity. One way to circumvent this problem is to use an incremental approach to linear elasticity. Using the incremental approach, the stress increment is calculated from strain increments encountered over a period in which the material properties are assumed to be constant. During subsequent increments the material properties may take on new values from which the new incremental stress values will be calculated. The final stress state of the resin is simply the addition of all the incremental stress values.

During the cure of an epoxy resin, the total strain in the resin comes from three sources. These strains include the mechanical strain, the linear shrinkage due to chemical reaction, and the thermal expansion or contraction due to temperature changes. The general equation for an ageing, linear thermoelastic material in differential form is given by:

$$E(T, p)\{d\varepsilon_{ij} - \delta_{ij}[\alpha(T, p)\,dT - \tau(T, p)\,dt]\}$$
$$= [1 + v(T, p)]\,d\sigma_{ij} - \delta_{ij}v(T, p)\,d\sigma_{kk} \quad (1)$$

where $d\sigma_{ij}$ is incremental stress, $d\varepsilon_{ij}$ is incremental strain, $E(T, p)$ is modulus as a function of temperature and

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extent of reaction, $\alpha(T, p)$ is thermal expansion coefficient as a function of temperature and extent of reaction, dT is temperature increment, dt is time increment, p is extent of reaction, $\tau(T, p)$ is linear rate of shrinkage due to reaction as a function of temperature and extent of reaction, $v(T, p)$ is Poisson's ratio as a function of temperature and extent of reaction, and δ_{ij} is the Kronecker delta.

Inherent in equation (1) are the following assumptions: material isotropy, incrementally linear elastic behaviour, history-dependent elastic coefficients and no viscoelastic behaviour. Since the equations are isotropic, shear stresses are not dependent upon shrinkage phenomenon.

The curing of epoxy resin under dimensional constraints, however, requires that equation (1) be modified to account for constrained conditions. If the constraining material is assumed to be rigid with perfect adhesion between the resin and constraining material, the mechanical strain increment is equal to zero. Therefore, if the epoxy resin is subjected to one-dimensional constraints, equation (1) reduces to:

$$d\sigma_{11} = -E(T, p)[\alpha(T, p)\,dT - \tau(T, p)\,dt] \qquad (2)$$

$$(d\sigma_{22} = d\sigma_{33} = 0,\ d\varepsilon_{11} = 0)$$

In studying equation (2), one can see that, at temperatures above the T_g of the resin where the modulus of the fully cured resin is approximately 30 MPa, the thermal stresses and shrinkage stresses will be insignificant. The thermal expansion coefficient of an epoxy resin increases by a factor of 3 as the resin is heated through its glass transition temperature. Upon cooling below T_g, however, the thermal stresses will be large due to the increase in modulus of the epoxy resin to approximately 3 GPa. Thus the 100-fold increase in modulus below T_g outweighs the effect of a factor of 3 decrease in the thermal expansion coefficient. Indeed this was shown to be the case by Vratsanos and Farris[6].

In *Figure 1* the thermal stresses developed in a uniaxially constrained epoxy resin are shown as the sample is cooled through the glass transition region. Very little internal stress is developed in the rubbery region owing to the low modulus of the resin. Below the glass transition temperature of 80°C, however, the thermal stress increases dramatically.

For a two-dimensionally, or biaxially, constrained sample, the stress in the constrained directions is given by:

$$d\sigma_{11} = d\sigma_{22} = \frac{-E(T, p)[\alpha(T, p)\,dT - \tau(T, p)\,dt]}{1 - v(T, p)} \qquad (3)$$

$$(d\sigma_{33} = 0,\ d\varepsilon_{11} = d\varepsilon_{22} = 0)$$

As in the one-dimensional case, the thermal and shrinkage stresses at temperatures above T_g will be insignificant. For example, in a coating the resin is free to move in the direction normal to the plane and the low modulus of the rubber-like resin will prevent significant stress build-up. Thermal stresses below T_g under biaxial constraints will be larger than those under uniaxial constraints by a factor of $1/(1-v)$. Below T_g where $v = 1/3$, this results in a 50% stress increase.

For a three-dimensionally constrained epoxy resin, the stress is given by the following equation:

$$d\sigma_{11} = d\sigma_{22} = d\sigma_{33} = \frac{-E(T, p)[\alpha(T, p)\,dT - \tau(T, p)\,dt]}{1 - 2v(T, p)}$$

$$= -K(T, p)[3\alpha(T, p)\,dT - 3\tau(T, p)\,dt]$$

$$(d\varepsilon_{11} = d\varepsilon_{22} = d\varepsilon_{33} = 0) \qquad (4)$$

where $K(T, p)$ is the bulk modulus as a function of temperature and extent of reaction. In this case the thermal and shrinkage stresses should be large at temperatures above T_g. For a crosslinked epoxy resin above its T_g, the behaviour is very similar to that of a rubber and Poisson's ratio approaches a value of 0.5. Thus, the value of the denominator in equation (4) tends towards zero, resulting in a large stress build-up for any temperature change or chemical reaction resulting in shrinkage. Equations (2) and (3) indicate that significant changes in stress can only result from large changes in apparent modulus, whereas equation (4) shows that large stresses are incurred regardless of the apparent modulus due to the volumetric constraints imposed on the material.

MATERIALS

The epoxy resin used in the study was Epon 828 (a diglycidyl ether of bisphenol-A resin) manufactured by the Shell Chemical Co. The curing agent used was Jeffamine T-403 (polyoxypropylenetriamine) manufactured by the Texaco Chemical Co.

EXPERIMENTAL

The epoxy resin and curing agent were mixed in a 1:1 ratio of amino hydrogens to epoxide groups. In order to remove dissolved gases, the mixture was placed under a vacuum. The glass transition temperature of the epoxy resin is 80°C, as determined by differential scanning calorimetry.

The epoxy resins were subjected to three-dimensional constraints by being cured in cylindrical stainless-steel tubes with a large length/diameter ratio. After gelation the epoxy is essentially three-dimensionally constrained within the tube. A 6 inch (~ 15 cm) length of 3/8 inch (~ 1 cm) SS-304 tubing with a wall thickness of 0.035 inch (~ 0.9 mm) was used as the constraining vessel.

Residual stresses in the epoxy resin were calculated from strain measurements of the tube surface. Resistance strain gauges were bonded longitudinally and tangentially to the tube surface. A reference tube filled only with neat
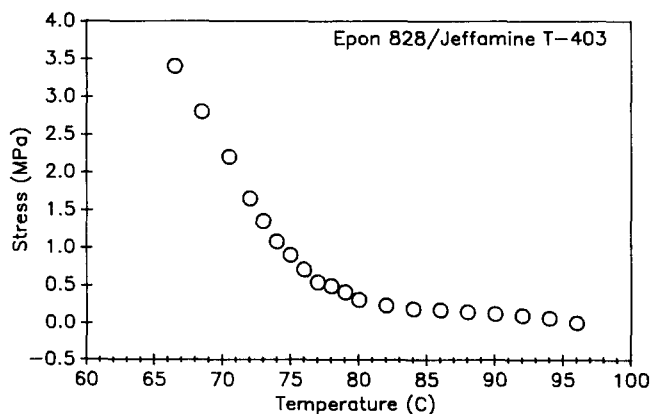

Figure 1 Stress *versus* temperature curve for a uniaxially constrained sample of Epon 828/Jeffamine T-403 during cooling through the glass transition region

Epon 828 and with strain gauges attached was used for temperature compensation. This allows the measurement of only mechanical strain due to the curing resin and not of the thermal strain due to temperature changes.

The measured mechanical strains were used to calculate the stresses on the surface of the steel tube from the following equations:

$$\bar{E}\bar{\varepsilon}_{\phi\phi} = \bar{\sigma}_{\phi\phi} - \bar{\nu}\bar{\sigma}_{zz} \qquad (5)$$

$$\bar{E}\bar{\varepsilon}_{zz} = \bar{\sigma}_{zz} - \bar{\nu}\bar{\sigma}_{\phi\phi} \qquad (6)$$

where the bars over the variables refer to the steel tube and the subscripts ϕ and z refer to the tangential and longitudinal directions, respectively. The radial stress is equal to zero on the outer surface of the steel tube. Handbook values for the Poisson's ratio (0.29) and tensile modulus (200 GPa) of SS-304 were used in the calculations.

The calculated tube stresses were used to calculate the internal stresses in the epoxy resin from the following cylindrical pressure vessel equations:

$$\sigma_{\phi\phi} = \sigma_{rr} = \bar{\sigma}_{\phi\phi}(b^2 - a^2)/2a^2 \qquad (7)$$

$$\sigma_{zz} = \bar{\sigma}_{zz}(b^2 - a^2)/a^2 \qquad (8)$$

where a and b refer to the inner and outer tube radii, respectively. According to linear elastic theory, $\bar{\sigma}_{\phi\phi} = \bar{\sigma}_{rr}$ on the inner wall of the tube and the boundary conditions imply that the stress on the inner wall is equal to the stress in the epoxy resin. Experiments have shown that $\sigma_{\phi\phi} = \sigma_{rr} = \sigma_{zz}$, indicating that the epoxy is under hydrostatic compression or tension.

RESULTS AND DISCUSSION

Prior to measuring stresses in the curing epoxy resin, qualitative observations of the epoxy resin cured in thick-walled glass tubes (o.d. = 7 mm, i.d. = 1 mm) were made. In one case the resin was cured isothermally at 100°C. Soon after gelation of the resin, cracks formed within the resin due to the shrinkage associated with the curing reaction. The epoxy-filled tube with cracks is shown in *Figure 2*. The formation of cracks within the epoxy resin occurred at all isothermal cure temperatures tested in the range from 50 to 110°C. The incidence of cracking, however, was not limited to the Epon 828/
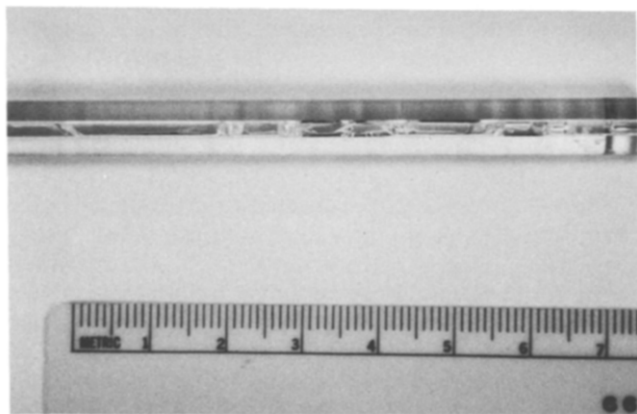

Figure 2 A three-dimensionally constrained sample of Epon 828/ Jeffamine T-403 cured isothermally at 100°C in a thick-walled glass tube. The cracks in the epoxy resin formed during the isothermal cure
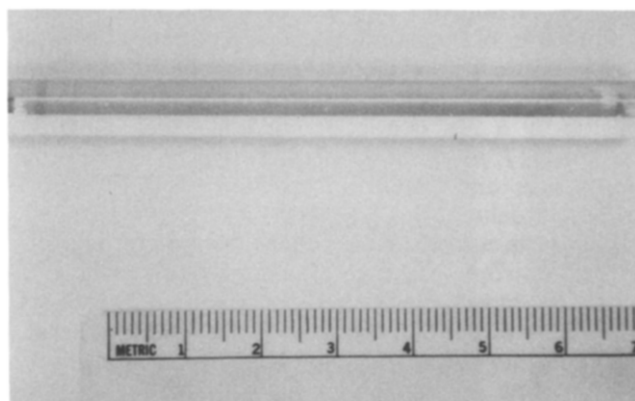

Figure 3 A three-dimensionally constrained sample of Epon 828/ Jeffamine T-403 cured using a ramped cure. No cracking or debonding of the epoxy resin occurred

Jeffamine T-403 system. Cracks were also observed in Epon 828 cured isothermally with curing agents such as diaminodiphenylsulphone (DDS) and piperidine at temperatures near the ultimate T_g of each system.

In order to alleviate the cracking problem, a different approach to curing the epoxy was employed. The cure schedule was developed by studying the time–temperature–transformation (TTT) diagrams developed by Gillham[14]. It was noticed that if an epoxy was cured for a long time at a constant temperature well below its ultimate T_g, the resin would only reach a state in which it would just achieve gelation and then vitrify. Since shrinkage stresses only build up after the resin has gelled, very little stress should be on the epoxy in this state. If the temperature were now increased in a linear ramp, the large thermal expansion coefficient of the gel should impart large compressive stresses on the resin, which in effect reduce the tension developed by polymerization shrinkage. Further increases in temperature, however, would cause the crosslinking reaction to continue, resulting in more shrinkage. This shrinkage would tend to counteract the compressive stress caused by thermal expansion.

Epoxy resins were cured in the glass tubes with a modified cure schedule. The resin was cured for 36 h at 30°C, then the temperature was increased at 10°C per hour to a final temperature of 100°C. The resin was held at 100°C for 2 h before being cooled to room temperature at 20°C per hour. This cure schedule resulted in a cured epoxy resin with no cracks and no debonding from the glass surface. A picture of the tube is shown in *Figure 3*.

After obtaining a qualitative picture of the large stresses that occur during the cure of an epoxy resin, the next step was to determine the magnitude of the residual stresses in the resin. Prior to measuring the stresses in a curing epoxy resin, however, the method and equations for determining internal pressures were tested by pressurizing the tube with nitrogen gas. The pressure was stepped up in several increments to a maximum pressure of 7 MPa. In all cases the calculated internal pressures from strain-gauge measurements were within 2% of the observed gauge pressure.

The first attempt to measure curing stresses in three-dimensionally constrained epoxy resins was made for a resin cured isothermally at 90°C. The ultimate T_g of the Epon 828/Jeffamine T-403 system is 80°C. Results from

previous experiments indicated that cracks would form in the resin and it was hoped that the stress at which these cracks formed could be determined. Unfortunately, this stress could not be determined due to a 10°C exotherm during the reaction, which made it impossible to separate the mechanical strain from the thermal strain caused by the exotherm. Curing the epoxy at temperatures well below the T_g of the resin would eliminate exotherm problems, as the reaction proceeds slowly enough to dissipate all of the heat generated, keeping the sample essentially isothermal.

The next attempt to measure residual stresses was made following a ramped cure schedule. In this experiment the resin was cured isothermally for 24 h at 40°C, followed by a 10°C per hour ramp to 90°C. The sample was held at 90°C for 2 h and then cooled at 20°C per hour down to 30°C. The calculated stress results for the experiment are shown in *Figure 4*.

During the 24 h isothermal cure at 40°C, the shrinkage stress increased to 8 MPa tension. Gelation occurred after 7 h, at which point the stress began increasing. The stress increased rapidly over the next 5 h before slowly levelling out during the remainder of the cure. A shrinkage stress of 8 MPa is much greater than that measured for an epoxy cured under one- or two-dimensional constraints. For the Epon 828/Jeffamine T-403 system cured under one-dimensional constraints using the method of Vratsanos and Farris[6], a value of 0.15 MPa was obtained. Others who have studied curing stresses in biaxially constrained coatings have reported negligible stresses due to the crosslinking reaction[4,5]. The explanation for the small stresses in uniaxially and biaxially constrained epoxy resins is the low modulus (30 MPa) of the fully cured resin in the rubbery region. In the three-dimensionally constrained epoxy, the Poisson's ratio approaches 0.5, indicating incompressible behaviour. Thus any desire to change in volume, as the curing reaction does, leads to a large stress increase.

Following the isothermal cure at 40°C, the resin is heated to 90°C at 10°C per hour. During the temperature ramp the resin goes from a state of tension into a state of compression. It is interesting to note that at 55°C a decrease in slope of the stress *versus* temperature curve occurs. Presumably, it is at this point where chemical reactions associated with continued cure commence and cause additional shrinkage of the resin. The change in slope occurred in every experiment of this type. The epoxy
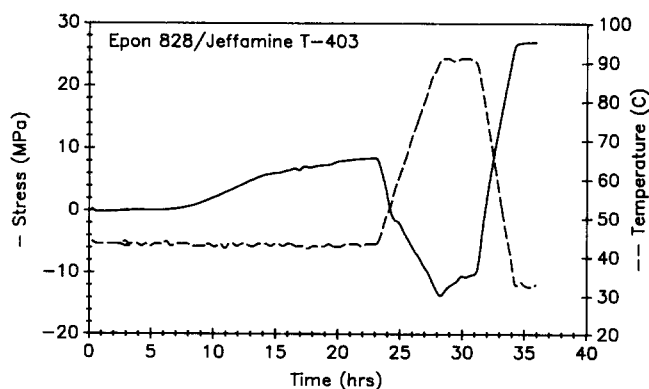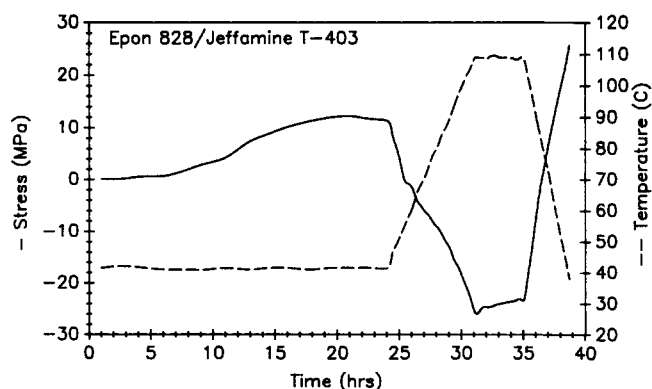
Figure 5 The stress (——) and temperature (- - - -) profiles of a three-dimensionally constrained sample of Epon 828/Jeffamine T-403 cured to 110°C
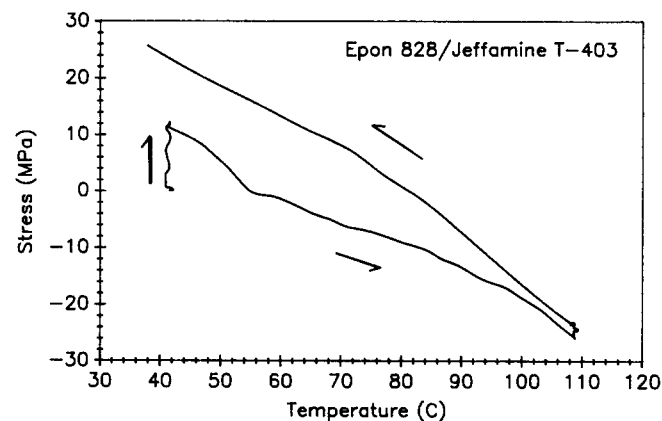
Figure 6 The stress *versus* temperature plot of a three-dimensionally constrained sample of Epon 828/Jeffamine T-403 cured to 110°C

resin was under 15 MPa compression at the end of the temperature ramp.

The resin was held at 90°C for 2 h during which time the compressive stress on the resin decreased to 10 MPa. The reduction in stress is probably due to further reaction of the epoxy resin and to shrinkage associated with physical ageing.

During the cool-down to 30°C, the stress in the epoxy resin went from a compressive stress of 10 MPa to a tensile stress of 25 MPa. It is interesting to note that only a slight change in the slope of the stress curve occurred as the epoxy was cooled through its T_g. In one- and two-dimensionally constrained samples the stress increases dramatically as the resin is cooled below T_g. In fact, the stress associated with curing and cooling the resin at temperatures above its T_g is neglected in the calculation of the residual stress of the resin. The only contribution to the residual stress is from the difference in the thermal expansion coefficients of the epoxy and the constraining material upon cooling below the glass transition temperature.

An experiment was performed in which the same cure schedule was repeated except that the temperature was ramped up to 110°C. The results of this experiment are shown in *Figure 5*. The results are nearly identical to those obtained for the ramp to 90°C except that the compressive stress at the end of the ramp is 28 MPa.

In *Figure 6* the results of the previous experiment are shown on a stress *versus* temperature plot. As one can see, there is a slight curve in the stress–temperature plot

Figure 4 The stress (——) and temperature (- - - -) profiles of a three-dimensionally constrained sample of Epon 828/Jeffamine T-403 cured to 90°C

as the sample was cooled through the glass transition temperature of the resin. The slope of this curve, however, is greater when the sample is above its T_g. Since the epoxy resin is volumetrically constrained, the implication of the small change in slope through the transition region is that the product of the bulk modulus and the bulk thermal expansion is nearly constant throughout the temperature range studied. This was explained above in the theory section because of the change in Poisson's ratio and modulus of the material. In the rubbery region the epoxy has a low modulus, but a Poisson's ratio close to 0.5 indicates incompressible behaviour. Thus in the volumetrically constrained state, large stresses are incurred above the glass transition temperature of the resin. In the glassy state, Poisson's ratio is approximately 0.33 but a modulus of 3 GPa leads to the build-up of large residual stresses.

The bulk modulus of the epxoy resin can be calculated from the results obtained during the experiment. Using the slope of the stress–temperature curve and the coefficients of thermal expansion of the steel tube (α_s) and the epoxy resin (α_e), the bulk modulus can be calculated from the following equation:

$$K_{3d} = (d\sigma/dT)/[3(\alpha_s - \alpha_e)] \qquad (9)$$

The bulk modulus values obtained with equation (9) were compared with those obtained from linear elastic theory through the following equation:

$$K_{et} = E/[3(1-2v)] \qquad (10)$$

The modulus was calculated from the initial slope of the stress–strain curve during a tensile test on the Epon 828/Jeffamine T-403 system. Poisson's ratio was measured with strain gauges as the absolute ratio of the transverse strain to the longitudinal strain during a tensile test.

The bulk modulus values calculated with both equations at various temperatures are shown in *Table 1*. Good agreement was obtained for the bulk modulus values

Table 1 Bulk modulus values of Epon 828/Jeffamine T-403 epoxy resin

Temperature (°C)	K_{et} (GPa)	K_{3d} (GPa)
26	2.9±0.3	3.3±0.5
55	3.1±0.3	2.8±0.4
105	–	1.6±0.2

calculated with equations (9) and (10). In general, the bulk modulus of the Epon 828/Jeffamine T-403 system decreases with increasing temperature. This decrease is expected due to the increase in the thermal expansion coefficient of the epoxy resin with increasing temperatures.

CONCLUSIONS

In this paper the residual stresses in a three-dimensionally constrained epoxy resin were measured. From the results obtained the following conclusions can be made.

Isothermal cures in three-dimensionally constrained epoxy resins lead to the formation of cracks within the resin.

Ramped cures help prevent the formation of cracks within the resin.

Tensile residual stresses as large as 28 MPa were measured in a fully cured epoxy resin subjected to three-dimensional constraints.

Large internal stresses developed during the cure of an epoxy resin above and below the glass transition temperature when the resin is volumetrically constrained.

ACKNOWLEDGEMENT

REFERENCES

1 Koroneos, E. G. *Colloid Polym. Sci.* 1978, **256**, 741
2 Srivastava, A. K. and White, J. R. *J. Appl. Polym. Sci.* 1984, **29**, 2155
3 Andonian, A. T. and Danyluk, S. *J. Mater. Sci.* 1985, **20**, 4459
4 Shimbo, M., Ochi, M. and Shigeta, Y. *J. Appl. Polym. Sci.* 1981, **26**, 2265
5 Wippler, C., Aboulfaraj, M., Schirrer, R. and Pixa, R. *Polym. Compos.* 1988, **9**, 125
6 Vratsanos, M. S. and Farris, R. J. *J. Appl. Polym. Sci.* 1987, **33**, 915
7 Cunningham, B., Sargent, J. P. and Ashbee, K. H. G. *J. Mater. Sci.* 1981, **16**, 620
8 Boriek, A. M., Akin, J. E. and Armeniades, C. D. *J. Compos. Mater.* 1988, **22**, 986
9 Hahn, H. T. and Pagano, N. J. *J. Compos. Mater.* 1975, **9**, 91
10 Hahn, H. T. *J. Compos. Mater.* 1976, **10**, 266
11 Harris, B. *J. Mater. Sci.* 1978, **13**, 173
12 Griffin, O. H. Jr *J. Compos. Mater.* 1983, **17**, 449
13 Griffin, O. H. Jr *J. Compos. Mater.* 1988, **22**, 53
14 Enns, J. B. and Gillham, J. K. *J. Appl. Polym. Sci.* 1983, **28**, 2567