CURING STRESSES IN THICK POLYMER COMPOSITE COMPONENTS PART I: ANALYSIS

M. R. Wisnom[1], L. G. Stringer[2], R. J. Hayman[2], and M. J. Hinton[2]

[1]*University of Bristol, Department of Aerospace Engineering, Bristol, BS8 1TR, U.K*
[2] *Mechanical Sciences Sector, DERA, Farnborough, Hants, GU14 0LX, U.K.*

SUMMARY: Residual stresses throughout the cure cycle in thick filament wound tubes are analysed considering the effects of thermal expansion, chemical shrinkage, orthotropic viscoelasticity, and the gelation and cure process. Good correlation with measured strains is obtained, but only if gelation is modelled. It is shown that interlaminar stresses during the cure cycle are generally low. However, if three dimensional constraint is present, significant stresses can arise due to the relatively high bulk modulus of the material even in the partially cured state. Since the strength is low early in the cure cycle, it is postulated that these stresses may be responsible for delamination.

KEYWORDS: Residual stresses, Cure modelling, Delamination, Finite element analysis, Filament winding.

INTRODUCTION

Residual stresses generated during the elevated temperature cure of thick section polymer composite components can lead to delamination. Hoop wound glass-epoxy tubes of inner diameter 100 mm have been found to contain extensive delamination for wall thicknesses of 42 mm or more, but no significant delamination for thicknesses of 30 mm or less [1]. The purpose of this research was to gain a better understanding of the reasons for delamination, and develop methods for predicting it. These could then be used to investigate ways to manage residual stresses in order to avoid delamination. This paper considers the theoretical analysis of stresses generated during the cure cycle, together with validation by comparing results with measurements from strain gauges embedded in filament wound tubes. A companion paper presents the experimental techniques which were used to produce data to input into the model and for correlation of results [2]. Management of residual stresses during the cure based on the insight gained from the analysis is also discussed [2].

Considerable research has been published on residual stresses [e.g. 3-7]. Much of this has focussed on thermal residual stresses during the cooldown of relatively thin laminates. Analysis of the stresses arising early in the cure cycle in thick composites raises many difficult issues, and requires considerable data which is difficult to obtain. It is also hard to measure residual stresses, and there is a need for further experimental data and correlation studies.

The generally accepted view is that residual stresses in polymer composites arise primarily due to the anisotropic thermal expansion of individual plies. In laminates containing multiple ply orientations, differential thermal contraction occurs during cooldown from the elevated temperature cure. Initial analysis therefore focused on these thermal stresses. The cooldown from 120°C to 20°C was analysed for a hoop wound tube using room temperature elastic properties for E glass/MY750 epoxy and assuming a uniform temperature distribution. The peak through-thickness tensile stress for a tube with inside and outside radii of 50 mm and 90 mm respectively was found to be only 2.8 MPa, not sufficient to cause delamination in the fully cured composite. The effect of non-uniform temperatures through the thickness was also investigated, and found to only marginally increase the peak stress. Modelling the contact between the mandrel and tube made some difference to the results, but stresses were still low.

These results led to the hypothesis that stresses arising in the cure cycle prior to cooldown may be responsible for delamination. Further analysis directed at this phase of the cure using the ABAQUS finite element program [8] is presented in this paper. An attempt has been made to model as many as possible of the factors influencing the generation of stresses: cure shrinkage as well as thermal strains, orthotropic viscoelasticity to account for relaxation of stresses, the effect of the changing glass transition temperature (Tg) during the cure, separate treatment of shear and bulk modulus effects, the process of gelation, cure kinetics, the exotherm and interaction between the tube and the mandrel.

HEAT TRANSFER ANALYSIS OF CURE CYCLE

A transient heat transfer analysis was undertaken of a thick hoop wound E glass/MY750 epoxy tube to determine the temperature history throughout the cure cycle. A simple cure kinetics model was incorporated in order to predict the degree of cure during the cycle. This allowed the effect of the exotherm to be included, and also meant that gelation and chemical shrinkage could be modelled in the subsequent stress analysis.

Material modelling

A simple micromechanics model was embedded within the overall finite element analysis, effectively representing the composite as a layered medium of alternating fibre and matrix materials. This was achieved by using separate elements for the fibre and matrix, allowing the orthotropic response of the composite to be modelled on the basis of the isotropic properties of the fibre and matrix. The standard ABAQUS isotropic viscoelastic analysis could then be used to model the orthotropic viscoelastic material. Each composite “element” therefore consisted of three finite elements, one for the fibre, and one each for the matrix on either side. The ratio of thickness of the fibre elements to the total thickness was based on the volume fraction of 71%. This approach was used to be consistent with the stress analysis, and gave the same results for the temperature distributions as an analysis using the equivalent homogeneous composite properties shown in Table 1. Resin and composite heat capacities were measured using DSC. Other properties are typical literature values.

Analysis details

A 2-D model was produced of a slice of a hoop wound glass-epoxy tube with inside and outside radii of 50 mm and 100 mm, representing an infinitely long tube with no end effects.

Table 1: Thermal properties for E glass/MY750 tube and steel mandrel

	Fibre	Matrix	Composite	Mandrel
Thermal conductivity ($Wm^{-1}K^{-1}$)	1.0	0.2	0.463	52
Specific heat capacity ($Jkg^{-1}K^{-1}$)	720	1800	900	460
Density ($kgmm^{-3}$)	$2.56x10^{-6}$	$1.25x10^{-6}$	$2.18x10^{-6}$	$7.85x10^{-6}$

The model consisted of a segment of one degree arc with a single row of eight noded DC2D8 elements. The tube was divided radially into 25 sets of "elements". A steel mandrel 5 mm thick was also modelled using six elements. The mesh is shown in Fig. 1.

Convective heat transfer was assumed at the surface of the tube, with the oven temperature following the cure cycle. A heat transfer coefficient of 30 $Wm^{-2}K^{-1}$ was used, estimated from the lag between the tube surface and oven temperatures. It was assumed that no heat transfer occurs at the inside of the mandrel. The slice model precludes any heat transfer in the axial or circumferential directions.

The phase before gelation is not of interest because no stresses develop. The analysis was therefore started at the beginning of the ramp from 90°C to 130°C. The oven temperature was held for 1.5 hours at 130°C , then ramped to 150°C , held for 2.5 hours and finally cooled to 20°C. All temperature changes were at a rate of 36°C/hour.

Cure kinetics

A very simple model of the cure kinetics of the MY750 resin was implemented in ABAQUS in the HETVAL user subroutine, treating the degree of cure, β, as a solution dependent state variable. Experimental data indicated that gelation occurred at an approximately constant temperature of 112°C, and so modelling of the development of the degree of cure started when this temperature was reached, assuming an initial value of 0.6 at gelation. A simple equation for the rate of change of cure with time was established based on Tg data from DMTA measurements and a relationship between Tg and degree of cure derived from molecular modelling studies:

$$d\beta/dt = 0.001(0.86-\beta)\exp[-350/T] \qquad (1)$$

where T is the temperature. Eqn 1 leads to a maximum degree of cure of 0.86, as defined by the molecular modelling. This simplified relationship does not capture the complex behaviour of the resin, but was nevertheless found to fit the available data quite well. Efforts are currently underway to develop a more sophisticated model of the cure kinetics.

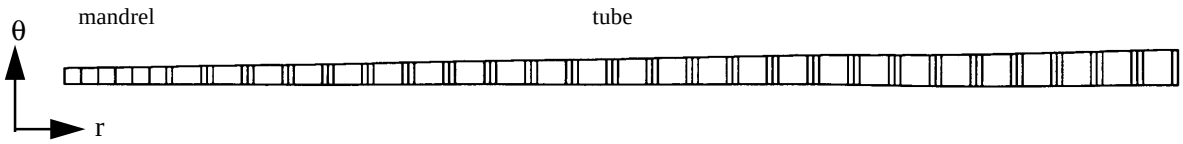
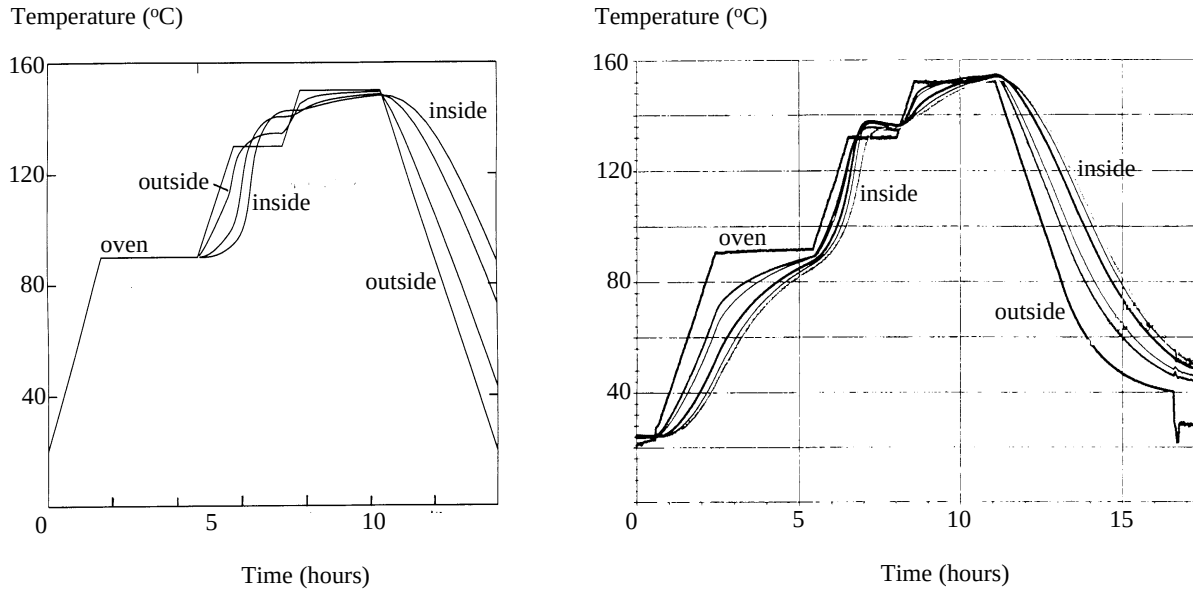


Fig. 1: Finite element model of slice of tube



a) analysis b) experimental

Fig. 2: Temperature time histories for cure of 50 mm thick hoop wound tube

The effect of the exotherm was included in the HETVAL subroutine by releasing an amount of heat of 278 J/g of resin over the range of degree of cure from 0.6 to 0.86. This value was based on DSC measurements.

Results

Fig. 2a shows the predicted temperature time history for points on the inside, centre and outside surface of the tube compared with the oven temperature. The experimental results are shown in Fig. 2b. The comparison is good except at the end of the cooldown where the oven temperature was not in fact controlled as closely as assumed in the analysis. There is slightly less overshoot in temperature at the start of the 130°C hold than predicted, which is believed to be due to the exotherm before gelation, which was not modelled.

STRESS ANALYSIS OF CURE CYCLE

A viscoelastic stress analysis of the cure cycle of the same hoop wound tube was carried out based on the temperature and degree of cure histories from the heat transfer analysis. The effect of gelation and the contact at the mandrel were included in the analysis.

Analysis details

The same mesh was used as for the heat transfer, but with CGPE10 generalised plane strain elements. These allow strain in the axial direction, but with a constant value controlled by an additional degree of freedom. The layered model assumes that in the fibre direction the hoop strains are the same in the fibre and matrix, whilst transverse to the fibres the radial stresses are the same. Equal fibre and matrix stresses in the axial direction along the length of the tube are enforced by means of additional constraint equations linking the axial strains in the fibre and matrix elements taking account of the volume fraction. There is not sufficient space to explain this fully, but it effectively implements a simple "rule of mixtures" approach within the finite element analysis. It should give a reasonable estimate of the composite properties, especially above Tg, and experimental investigation of this is planned. All displacements in the circumferential direction were restrained to represent the axisymmetric condition imposed by the rest of the tube.

Viscoelasticity

Initially it was expected that the viscoelastic response of the composite would be important, and so the model was set up to be able to include this effect. The Williams-Landel-Ferry equation was used to relate the relaxation time to the temperature and Tg for the elements representing the matrix. This was linked to the degree of cure based on the relationship between Tg and degree of cure established from molecular modelling.

When the data was available and the analysis was run it was found that the Tg of the matrix remained below the cure temperature until the cooldown. Stresses therefore decayed rapidly, and the results were the same as for an elastic analysis with fully relaxed properties throughout the early part of the cycle. The viscoelastic parameters used are therefore not important, and will not be discussed further. It should be noted that this result is specific to the particular resin used. A similar effect may occur in some other resins, but for many materials the Tg will rise above the cure temperature, and so viscoelastic effects may become important earlier in the cycle.

Fully relaxed elastic properties

It is very important to take account of the different behaviour of the material under hydrostatic and shear stresses. It is commonly assumed that above Tg stresses are negligible because the effective modulus is low due to viscoelastic relaxation. This is generally a reasonable assumption for shear stresses. However the bulk modulus of epoxy typically decays by only a factor of two. Appreciable stresses can therefore arise whilst the material is above its Tg if there is constraint on volume changes.

This is normally handled in a viscoelastic analysis by separating the deviatoric and hydrostatic response and using different parameters for the relaxation of the shear and bulk moduli. For an elastic analysis with fully relaxed properties it is the Poisson's ratio that is crucial in determining the bulk response, and use of an appropriate value is essential.

The initial Young's modulus of the matrix measured well below Tg is 3.69 GPa, with a Poisson's ratio of 0.35. This corresponds to a bulk modulus of 4.1 GPa. The equilibrium shear modulus was taken as 0.6% of its initial value based on tests well above Tg, and the bulk modulus was assumed to decay to 50% of its initial value. The fibre was treated as elastic, with a modulus of 76.2 GPa and Poisson's ratio of 0.24. Test cases with uniform stresses gave

identical results using this data with the layered micromechanics model and using the equivalent homogeneous properties for the composite given in Table 2. The details of the implementation with fibre and matrix elements are therefore not important, and it can be considered simply as an orthotropic elastic analysis with fully relaxed properties. Note, the high value of Poisson's ratio, ν_{23}, is due to the relative incompressibility of the material together with the high stiffness in the fibre direction.

Table 2: Effective fully relaxed thermoelastic properties for E glass/MY750

Fibre direction modulus, E_1 (GPa)	54.1
Transverse moduli, E_2, E_3 (MPa)	112.5
Poisson's ratios ν_{12}, ν_{13}	0.3148
Poisson's ratio ν_{23}	0.9909
Shear moduli G_{12}, G_{13}, G_{23} (MPa)	28.3
Fibre direction thermal expansion coefficient, α_1 (K^{-1})	5.08×10^{-6}
Transverse thermal expansion coefficient, α_2 (K^{-1})	107.1×10^{-6}

Table 3: Thermoelastic properties for steel mandrel

Young's modulus (GPa)	207
Poisson's ratio	0.3
Thermal expansion coefficient (K^{-1})	11×10^{-6}

The moduli were assumed not to vary with degree of cure. This is a reasonable assumption for the bulk modulus, but less satisfactory for the shear modulus [7]. However, since bulk modulus effects were expected to be predominant, this was considered acceptable. The mandrel properties are given in Table 3.

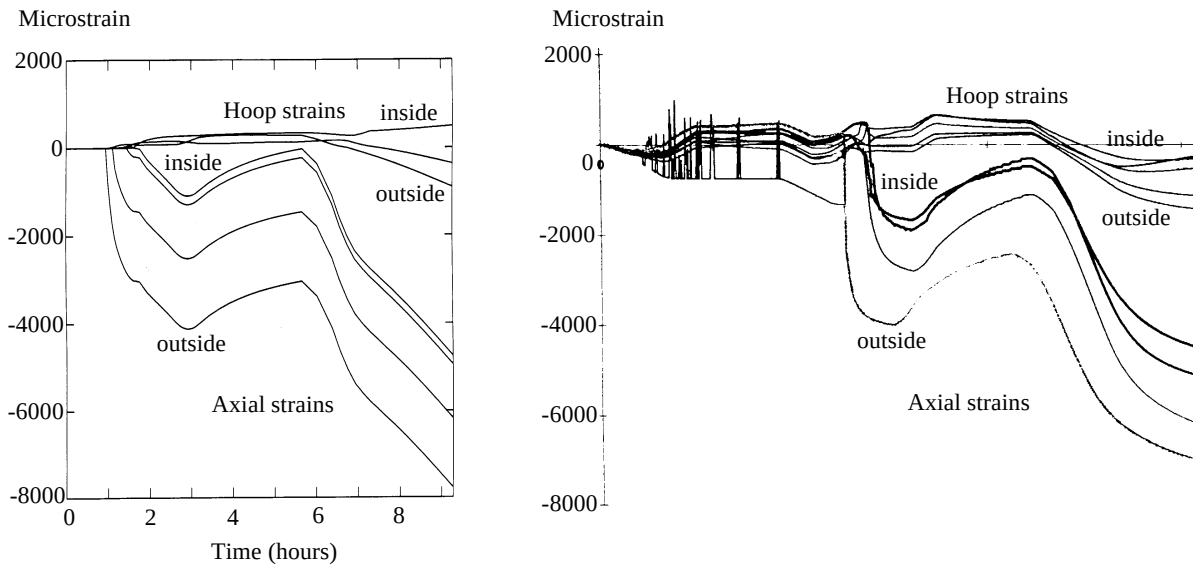
Volume changes

The expansion coefficient of the matrix changes by a factor of about three around Tg. Care is therefore needed to deal correctly with thermal expansion when both the temperature and the Tg are varying during the analysis. In the present case the interest is on the phase when the matrix is above its Tg, and so a typical value of the rubbery thermal expansion coefficient of 240×10^{-6} K^{-1} was used. The expansion coefficient of the fibre was taken as 5.05×10^{-6} K^{-1}. The equivalent orthotropic expansion coefficients for the composite are given in Table 2.

Chemical shrinkage was modelled with a total reduction in volume of 3.54% over the range of degrees of cure from 0.6 to 0.86. This was an initial estimate, and tests are planned to measure the shrinkage. Volume changes were implemented in ABAQUS by means of the UEXPAN user subroutine making use of the degree of cure read in as a field variable from the heat transfer analysis.

Modelling of gelation

It is essential to model gelation because it is only at this point that measurable stresses and strains start to develop. Before the resin gels, embedded strain gauges are not bonded to the material. At this stage only the response of the gauges will be recorded. Once gelation has occurred they will start to register the actual strain in the composite [1]. Initial attempts to model the cure without accounting for this gave strains that did not match the experimental results at all.



a) analysis b) experimental

Fig. 3: Strain time histories during cure of 50 mm hoop wound tube

Gelation was modelled by introducing extra viscoelastic terms so that all stresses relaxed completely if the degree of cure was less than 0.6. It was also necessary to specify no thermal strains prior to gelation so that the results could be compared directly with strain gauge readings.

Normally with a generalised plane strain analysis it would be assumed that the axial strains are constant over the whole model. However, before gelation, relative axial motion can occur as resin flows. To allow this all the elements were given different degrees of freedom in the axial direction so that initially they could act independently. User defined constraint equations were then imposed between adjacent elements which forced them to have the same incremental axial strains after both elements had gelled.

Interaction between the mandrel and tube

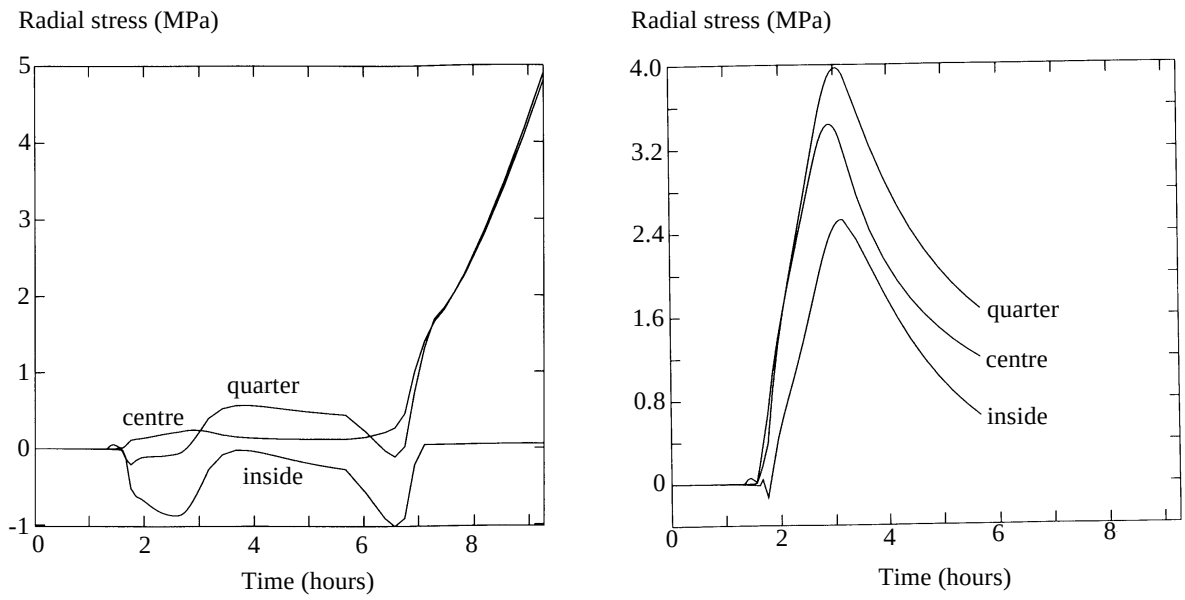
In the initial analysis the mandrel and tube were assumed to stay in contact. Duplicate coincident nodes on either side of the interface were connected directly together in the radial direction. Axial displacements were connected with a multi point constraint equation once the degree of cure of the first tube element exceeded 0.6. This allowed the effect of flow in the axial direction prior to gelation to be represented.

Large tensile stresses developed at the interface and so a second analysis was performed where contact elements were placed between the mandrel and tube. These allowed compressive

forces to be transmitted, but separated as soon as the radial stresses became tensile. No constraint was imposed in the axial direction, effectively modelling a frictionless interface.

Results

Fig. 3a shows the axial and hoop strains for the case with separation allowed at the mandrel. Note that the time is from the beginning of the analysis rather than from the start of the cure.



a) tube free to slip at mandrel

b) tube locked to mandrel

Fig. 4: Predicted through thickness stresses during cure of 50 mm thick hoop wound tube

The results compare well with the strain gauge measurements in Fig. 3b. There is a sharp axial contraction at the outside as soon as gelation occurs. The inside gels later, with a much smaller axial strain. The contractions reach a maximum and then the tube starts to expand axially due to thermal expansion as the temperature is ramped up and held at 150°C. The strains at the inside and outside now change together since the whole tube has gelled. Further contraction occurs during the cooldown. All these trends follow closely the experimental results.

Fig. 4a shows the radial stresses for this case. Values are low and mostly compressive until the cooldown. Fig. 4b shows the results for the early part of the cure for the case where the tube is fixed to the mandrel, corresponding to the situation before separation occurs. Significant radial tensile stresses develop due to the three dimensional constraint provided by the mandrel in the axial and radial directions and by the fibres in the hoop direction. The change in volume due to chemical shrinkage produces these stresses because the bulk modulus is relatively high even at this early stage in the cure cycle.

Once the stresses at the interface become tensile, separation would occur, and so the results after this point are not realistic, and would revert to those shown in Fig. 4a. However, there is a lag between tensile stresses developing inside the tube and those at the mandrel, with values around 1 MPa arising at the point when separation would be expected. This is a relatively high

value at such an early point in the cure before the strength has developed, and it is postulated that these stresses may be responsible for the delamination observed in thick tubes.

DISCUSSION

The results show the importance of modelling gelation, and allowing resin flow prior to the gel point, which is rarely considered in residual stress analyses. If this is ignored, the axial strains at different points through the thickness would all be the same, and the strong effect of differential contraction seen in the experimental results would not be reproduced.

The results also show the importance of bulk modulus effects, which can lead to significant stresses early in the cure cycle even when the Young's modulus is very low. Constraint effects such as the interaction between the tube and the mandrel therefore become crucial.

Analysis of different tubes showed that stresses reduced with decreasing thickness, consistent with the experimental observation of delamination only occurring on thick tubes. For a 3 mm thick hoop wound tube no significant tensile stresses developed at the interface, and so separation and slip at the mandrel would not be expected. The analysis therefore predicted no large axial contraction for this case, and this matched the experimental result.

The key to eliminating delamination early in the cure is to avoid tensile stresses developing. This can be done by balancing thermal expansion and chemical shrinkage. Constraint can be beneficial if stresses can be kept compressive, but if shrinkage predominates then constraint may give rise to hydrostatic tensile stresses which could initiate delamination. The model was used to investigate a number of options to reduce the susceptibility to delamination, and these are discussed in the companion paper [2].

The results obtained here were all based on preliminary data, and efforts are continuing to measure the critical parameters [2]. More detailed correlations with experimental data can then be made.

CONCLUSIONS

Thermal residual stresses during the cooldown of a thick hoop wound glass-epoxy tube were found to be too small to be a likely cause of delamination, and it is therefore necessary to consider stresses arising earlier in the curing process.

An analysis approach has been developed which takes account of the critical phenomena responsible for generating residual stresses throughout the cure cycle. The important issues for the analysis are the correct representation of the volume changes occurring during the cure, accurate modelling of constraint and appropriate treatment of bulk modulus effects. For the resin considered, viscoelastic effects proved to be unimportant, and an elastic analysis with fully relaxed properties is adequate.

Initial results from the model gave good correlation with thermocouple and strain gauge data from instrumented tubes. This could only be achieved by modelling gelation. The analysis showed that stresses are generally low early in the cure cycle. However, significant stresses can arise if three dimensional constraint is present due to the relatively high bulk modulus even

in the partially cured state. The mandrel is an important source of constraint. Stresses increase with thickness, with radial tension of about 1 MPa for a 50 mm thick 100 mm inside diameter tube. Since the strength is low at this point in the cycle, these stresses may cause delamination.

ACKNOWLEDGEMENTS

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INITIAL ANALYSIS OF THERMAL RESIDUAL STRESSES

It is generally accepted that residual stresses in polymer composites arise primarily due to the anisotropic thermal expansion of individual plies. In structural laminates containing multiple ply orientations, differential thermal contraction occurs during cooldown from the elevated temperature cure. Initial analysis therefore focused on thermal stresses during this cooldown phase.

A model was produced of a slice of a hoop wound glass-epoxy tube with inside and outside radii of 50 mm and 90 mm. The model consisted of a segment of 1 degree with a single row of 16 generalised plane strain elements, as shown in Fig. 1. These allow strain in the axial direction, but with a constant value, representing the effect of a long, unconstrained tube away from its ends. The ABAQUS finite element program was used for the analysis [7], with CGPE10 elements with quadratic displacement functions. All displacements in the circumferential direction were restrained to represent the axisymetric condition imposed by the rest of the tube.

Cooldown from 120°C to 20°C was analysed using the room temperature elastic properties for E glass/MY750 shown in Table 1, and assuming a uniform temperature throughout the tube.

The distribution of through-thickness tensile stresses is shown in Fig. 2. The peak value is only 2.8 MPa; not sufficient to cause delamination in the fully cured composite. The results are compared with those from the analytical solution of Tarnopolskii [-], which is based on plane stress. The slight difference is due to the effect of axial stresses, which are ignored in the analytical solution.

The effect of non-uniform temperatures through the thickness was also investigated, and found to only marginally increase the peak stress. Modelling the mandrel made some difference to the results, but stresses were still low.

These results led to the hypothesis that stresses arising in the cure cycle <u>prior to cooldown</u> may be responsible for delamination. Further analysis was directed at this phase of the cure.

Initially there is considerable lag between the tube and oven temperatures, especially at the inner surface. Once the 130°C hold has been reached the interior temperatures continue to increase beyond this level due to the effect of the exotherm. The temperatures approach equilibriun values with the inside at a higher temperature than the outside, due to the assumption of no heat transfer at the mandrel. In the ramp to 150°C the outside temperature rises above that inside, and more rapidly approaches the oven temperature. On the cooldown there is an increasingly large lag between the temperatures at the inner and outer surfaces of the tube.

Tarnopolskii and Beil provide a good summary discussing the generation of stresses during filament winding and give some analytical solutions [3]. Lee and Springer developed a process model including thermochemical effects of curing and heat transfer, the change in fibre tension during processing and the generation of residual stresses and strains [4]. Good correlation was obtained with measurements of temperature and strains for thin cylinders [5]. Large stresses were predicted for thick cylinders [6], although these were not directly correlated with

experimental results. Bogetti and Gillespie used a similar elastic analysis approach for thick flat plates, and obtained good correlation for temperatures [7,8]. White and Hahn studied thin cylinders taking account of viscoelastic effects [9,10]. Corden et al considered the mechanisms of cracking in thick cylinders produced by resin transfer moulding [11]. Adolf and Martin presented a general model for the evolution of stresses in epoxy during the cure which addresses a number of the fundamental problems that need to be considered in the analysis [12].

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