CURING STRESSES IN THICK POLYMER COMPOSITE COMPONENTS PART II : MANAGEMENT OF RESIDUAL STRESSES

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

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

SUMMARY: Residual stresses during the cure of thick fibre reinforced composites can lead to delamination cracking and distortion of fibres during component manufacture. Residual stresses are generated by anisotropic thermal expansion behaviour, and also by chemical shrinkage of the resin. This is the second of two complementary papers. Part I described the development of a theoretical model to predict the level of residual stress during the composite cure process. Part II outlines some of the experimental techniques being used to validate the model and to incorporate further refinements (including modelling of the resin cure kinetics). Finally, progress in developing fabrication processes for managing the cure stresses without incurring delamination is presented. The fabrication processes investigated were filament winding and resin transfer moulding. The same materials, E-glass fibres and MY750 epoxy resin, were used for each.

KEYWORDS: Residual stresses, Residual strains, Epoxy cure, Delamination, Filament winding, RTM, Cure kinetics, Bragg gratings, Di-electric sensors.

INTRODUCTION

Fibre reinforced polymer composites are being used in structures to carry ever larger loads. As a consequence, become used in higher load bearing structures, composite thicknesses are increasing and manufacturing problems multiply. Curing of thick fibre reinforced composites can lead to delamination cracking and distortion of fibres during component manufacture, and this is exacerbated by the use of hot cure matrix resin systems. These problems occur as a result of residual stresses arising during the manufacturing process. Residual stresses are generated by anisotropic thermal expansion behaviour, and also by chemical shrinkage of the resin [1-3]. Thick section parts are usually too rigid for residual stresses to relieve by distortion, and so internal damage is more likely to occur.

The number of factors which need to be taken into account is large, and on-going work at DERA is investigating these issues both experimentally and theoretically. The aim is to gain a full understanding of fundamental principles responsible for the initiation of stresses during the fabrication of composite parts. This should allow ‘management’ of these stresses (including the generation of beneficial pre-stress) by optimisation of processing conditions. This is one of two complementary papers on the subject of cure stresses in thick composite

parts. The first paper [2], which is also presented at this forum, describes the development of a finite element model for predicting the three-dimensional residual stress state during the entire composite cure process. The model suggests that stresses can be managed by changing the cure cycle to alter the balance between chemical shrinkage and thermal expansion of the matrix resin. The influence of three dimensional shrinkage constraint is also taken into account by the model, and this is particularly relevant to processes such as filament winding and RTM, where mandrel and mould may provide this constraint. The current paper, part II of these complementary papers, outlines some of the experimental techniques being used to validate the model, and also describes experiments to refine the required modelling input data. Finally, progress in experimentally managing the cure stresses without incurring delamination model is presented.

EXPERIMENTAL

Materials and processing

To provide validation data for the model, and to highlight any process dependent effects, two fabrication processes were investigated; filament winding (FW) to produce simple cylinders, and resin transfer moulding (RTM) to produce flat panels. These processes were chosen as they are commonly used for manufacturing thick high-performance composite components, yet they allowed a similar range of component thicknesses and the same basic material components and lay-up. These were unidirectional E-glass fibres and Ciba Geigy MY750/HY917/DY073 resin system. MY750 is a widely used manufacturing epoxy resin with an upper cure temperature of 150°C. The same standard cure cycle was used in the current work for all components irrespective of their thickness. This E-glass/MY750 system has been researched extensively by DERA over the last 25 years [3-7].

The filament wound components were tubes of 100mm internal diameter and thickness ranging from 3mm to 55mm. All had the fibre reinforcement in the hoop direction. Flat panels were produced using the RTM process with 400mm x 410mm uni-directional E-glass fabric and ranged from 3mm to 50mm in thickness. All tooling, i.e. mandrel and moulds were steel. Further details of the materials and component sizes can be found in an earlier publication [1].

Strain measurement

Strain outputs from the FE model were correlated directly with experimental strains.

Embedded strain gauges - Strains were measured throughout the cure process using embedded strain gauges within filament wound (FW) tubes and RTM panels. Gauges were positioned in the fibre direction and transverse to the fibre direction. Thermocouples were included adjacent to each gauge position to measure the local temperature during cure. A titanium silicate block with attached reference gauges enabled thermal compensation of the recorded strain data. Again, further details are reported in Reference 1.

Optical Bragg gratings – These are being investigated as an alternative to strain gauges. Bragg sensor systems rely on the response of a Bragg sensor at a particular Bragg wavelength having a known (and predictable) response. It is accepted that the wavelength response of a Bragg grating to strain is of the form:

$$\frac{dl}{l_0} = C\frac{dL}{L}$$

where $\delta L/L$ = strain (ε), λ_0 = Bragg wavelength at zero strain, C is a constant, and $\delta\lambda/\lambda_0$ = change in Bragg wavelength with initial wavelength.

A polyimide coated Bragg grating OFS, with a centre wavelength of 1549.34 nm was embedded midway along a FW tube, orthogonal to the reinforcing fibre winding direction. The optical spectra was measured before and after curing of the composite, and the results shown in Fig. 1.

This wavelength shift of the Bragg wavelength corresponds to a strain (compressive), after correction for a small thermally induced strain, of 4725 μstrain (0.472 %). This compares extremely closely with the final strain gauge reading of 4748μstrain recorded in the adjacent strain gauge (see ¾ position gauge in Fig.7). The smaller peak is due to stress-induced birefringence in the optical fibre.

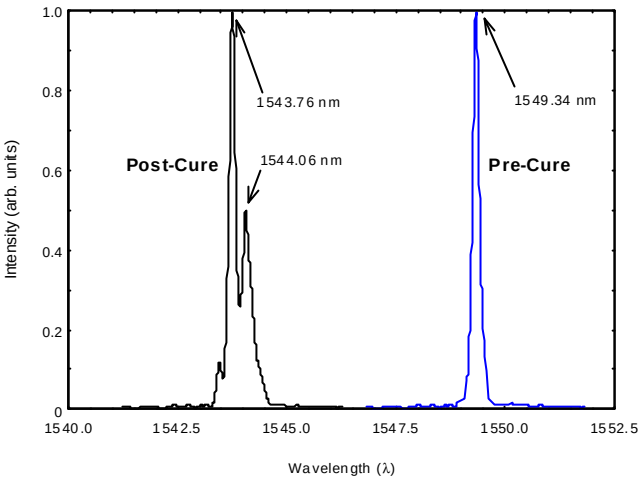

Fig.1 Optical Spectra of embedded Bragg grating before and after cure of filament wound tube

Compared to monitoring residual stresses using embedded electrical resistance strain gauges, fibre optic strain sensors have the advantage of being more simple to install and more compact. This is because strain gauges have to be individually installed and wired, whereas many Bragg gratings can be etched onto a single fibre optic cable. The installed fibre optic cable is also more compact than strain gauge and wire, and will offer less disturbance to the host composite.

Dielectric analysis of cure state

This will allow on-line monitoring of the state of cure of epoxy based composites, which will be beneficial in the development of a fully mature residual stress model. Miniature dielectric sensors, measuring 18mm x 10mm, have been fabricated for thick section composites via a photolithographic process [see Ref. 8].

The dielectric sensor was embedded in a 50mm thick FW tube alongside an existing thermocouple and strain gauge. A Solartron 1255 impedance analyser was used to interrogate the sensor. The form of the data interpreted from the sensor is shown below in Fig.2, for an isothermal cure of MY750. This data represents the magnitude of the imaginary impedance versus analyser frequency and time during cure. It can clearly be seen that the resonance peak and amplitude vary considerably with .the cure reaction.

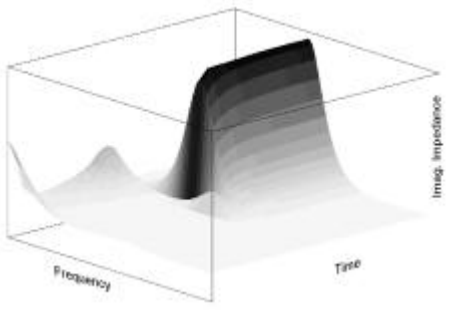

Figure 2 – dielectric impedance data in 'raw' form

The raw data format is relatively cumbersome and can be reduced to key parameters versus time. Two of the most important are the resonance peak frequency and amplitude with time. The processed results from the sensor embedded within the thick-section composite are shown alongside the data from the embedded thermocouple in Figure 3 *a* and *b*. The technique is not affected by temperature, as shown by the constant impedance parameters after vitrification.

It can be seen from the dielectric data that key cure information may be obtained from a relatively simple and inexpensive measurement technique. Currently work is in progress to quantify cure state from on-line analysis of the sensor signals.

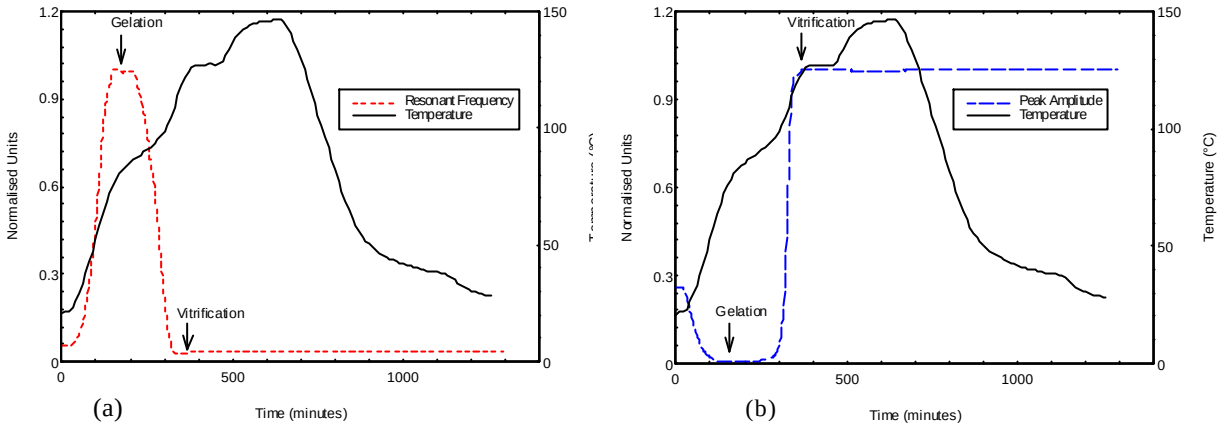

Figure 3 Dielectric data (a) resonance frequency (b) resonance amplitide

Input data for the 3D stress model

As described in the complementary paper [2], when focused only on thermal stresses during cooldown from the elevated cure temperature the stress model predicted a low through-thickness tensile stress of around 3MPa. This level of predicted stress was not sufficient to cause delamination in a fully cured composite. A fundamental consideration of the mechanisms involved during the curing process of a composite component led to the hypothesis (since supported by the work of Corden, Jones et al [9]) that stresses arising in the cure cycle prior to cooldown may be responsible for delamination. This hypothesis eventually led to a comprehensive list of resin and composite properties, and a knowledge of these parameters was required not just in the fully cured state but throughout the cure cycle.

The most critical of these parameters were thought to be cure kinetics and volumetric shrinkage. Also, the through-thickness tensile strength of the composite is required for comparing the predicted stress with the strength of the composite at the same point in the cure cycle.

Cure modelling and kinetics – The epoxy cure is being modelled using the DRYADD software from Oxford Materials Ltd [10]. It uses Monte-Carlo simulations rather than mathematical expressions. The types of molecules present, the reactions that may occur and the relative rates of these reactions (or actual kinetic rates if available) must be specified. The model provides information on the extent of reaction, which includes the various molecular weights in the sol and gel fractions, the number of crosslink sites, and the elastically active fraction in the gel.

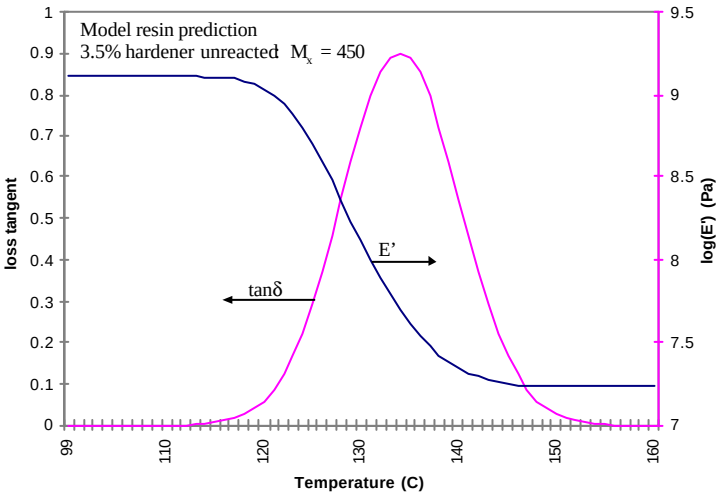

Fig.4 Prediction of Tg, loss tangent and elastic modulus from Group Interaction Modelling

The eventual objective is to obtain a detailed understanding of the physico-chemical processes during the cure of commercial epoxy systems. The aim is to be able to predict the number of all the different molecules in the polymer at all stages in the cure cycle. The most important molecular types are: unreacted monomers, pendant groups on the main chain backbone, and the elastically active crosslinked gel fraction.

The molecular composition predictions of DRYADD can then be used as input parameters to calculate the physical properties of the polymer through its cure cycle by means of structure-property relations of Group Interaction Modelling [11]. Each type of molecule is assigned a self-consistent set of physical parameters (cohesive energy, volume, heat capacity), which as used in a series of expressions to calculate properties such as the glass transition temperature, the visco-elastic properties of elastic modulus and loss tangent, and the thermal expansion coefficient. Typical predictions are shown in Fig.4 and these properties are calculated as a function of temperature, which allows experimental measurements such as DSC and DMTA to be made on resins through their cure history to monitor the reactions and to validate the model.

Eventually, through this iterative process of, experimental determination of kinetic rate constants, DRYADD modelling and Group Interaction Modelling it will be possible to predict the properties at any stage in the cure cycle. It will also be possible to predict the effect on properties of variations from the standard cure cycle, which may be required in order to properly manage the residual stresses.

Partially cured composite strength – flat panels representative of the FW E-glass/MY750 tubes were produced by filament winding on to a flat mandrel and subsequently curing by hot pressing. The cure process for each panel was halted at a key stage and the panel immediately removed to a freezer in order to arrest the degree of cure. Transverse tension tests were carried out on these panels at temperatures corresponding to the particular cure stage at which the panels had been removed, in conjunction with comparative ambient tests, to assess residual stresses.

The results of partially cure strength levels are depicted against cure schedule in Figure 5 (average of 5 specimens for each result). The minimum strength of those specimens tested was 2.86MPa and this occurred at the beginning of the +150^{o}C cure stage.

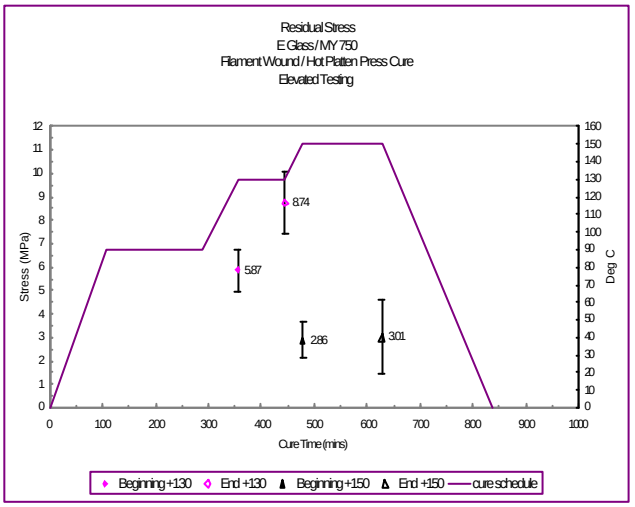

Fig.5 Partially cured transverse composite strengths at various points in the cure cycle

RESULTS AND DISCUSSION

Measured strains during cure

The earlier publication [1] discussed in detail the measurement of strains using embedded strain gauges. The strain gauges only measured meaningful strains after gelation. Before this, no physical bond exits between the strain gauges and resin, and there is no significant bonding between the matrix resin and reinforcing fibres. Without bonding no internal stresses can arise and the resin is free to flow. At gelation the resin solidifies, forming bonds to the embedded fibres and also to the gauges. It is at this point that meaningful internal strains can then exist.

Strains recorded in the fibre direction were positive throughout cure for all components. They showed a common trend dominated by thermal expansion effects. The magnitude of these fibre direction strains was similar for the range of component thickness produced.

In the thin components (3 mm), strains transverse to the fibre direction were also dominated by thermal expansion effects. Strains in the transverse direction were greater than those in the fibre direction and there was little variation through the thickness of the component. Fig.6 shows the strains for a 3mm thick FW tube, the dotted lines are the axial strains (i.e. perpendicular to the fibres) and the solid lines are hoop strains. Gauges were embedded at the inner (one fibre covering), quarter thickness, half thickness, three-quarter thickness and external (one fibre covering from the outer surface) tube positions, all gauges at the centre point along the axis of the tube.

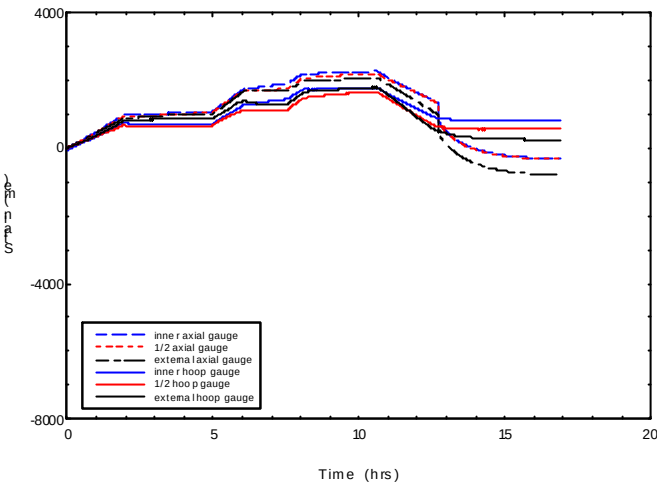

Fig.6 Hoop and axial strains in 3mm thick tube

Above 11 mm tube thickness a very pronounced feature was seen in the transverse strains. A sudden compressive strain was recorded as the resin gelled, which was attributed to shrinkage in the matrix resin. Fig.7 shows data for a 55mm thick tube. The strain curves represent the same orientation and position of gauges as in Figure 6.

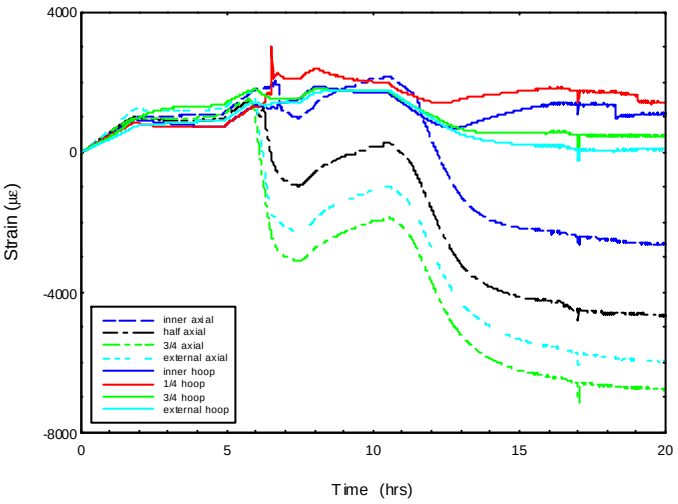

Fig.7 Hoop and axial strains in 55mm thick tube

Although shrinkage is a three-dimensional process it manifests itself in the transverse direction due to the low level of constraint, compared to fibre and tooling constraints in the other directions. In the latter stages of cure, after shrinkage was complete, the development of strains was predominantly due to thermal effects. The residual transverse strains were generally negative and increased in magnitude with increasing component thickness up to a maximum at 42 mm. Above this thickness the average residual strains stayed constant but varied significantly through the thickness.

All components were ultrasonically C-scanned after manufacture. Both tubes and panels of 30mm thickness and below showed no damage. Components thicker than this were found to contain significant levels of delamination.

A comparison between the model and experiment revealed a good fit between predicted and measured strains through the cure cycle, and this was discussed in the complementary paper [2]. The magnitude of the predicted radial stress also agreed reasonably well with that exhibited by some of the partially cured transverse tensile specimens in Fig.5. Although the

lowest measured strength of ~2.9MPa was at the start of the 150°C dwell, the very lowest strength was probably just after dwell, but this was difficult to ascertain experimentally.

Why there should be a spread of measured axial strains, as illustrated in Figure 7, becomes apparent when thermocouple temperatures are considered for each strain gauge location through the composite thickness. The curing oven temperature was set to the manufacturers recommended cure cycle (see Fig.5). In an earlier publication [1] it was shown that, for the thicker FW specimens, the thermal lag between inner and outer temperatures is very large. Oven curing is by convective heat transfer to the outside of the component, and this led to temperature differences across the composite tube as large as 36°C. For the RTM panels, where heat is transferred directly from platens on either side of the panel, the difference is quite small. If the processing conditions and composite thickness result in a temperature lag this causes a variable state of cure throughout the thickness of the composite during the cure cycle. A fully developed 3D residual stress model must therefore include the precise state of resin cure at any location in the composite at any moment in time. The resin cure kinetics modelling described earlier will provide this element of the stress model in due course.

Management of residual stresses

As discussed in the complementary paper [2] the key issue in preventing delamination is to avoid significant interlaminar tensile stresses developing. As we are concerned with delamination early in the cure cycle, when the strength of the material is low, it would be preferable to eliminate tensile stresses altogether if possible. Residual stresses arise because of constrained thermal expansion and chemical shrinkage. The fundamental way to manage the generation of stresses is therefore to match the thermal expansion and chemical shrinkage so as to minimise changes in volume early in the cure.

Stresses only arise if volume changes are constrained. Since the Young's modulus and shear modulus of the resin is very low early in the cure, significant stresses can only occur due to hydrostatic tension, and this requires constraint to be present in all three directions. In the filament winding process the mandrel can produce three-dimensional constraint if slippage between mandrel and composite is prevented. The residual stresses arising may not necessarily be deleterious, but may be arranged to be beneficial. Various options for stress management are being considered, some of which are designed prevent mandrel separation (or, in the case of RTM, mould separation), and some by allowing mandrel separation.

Use of a heated mandrel, with the mandrel heated using the same temperature history as the oven, is predicted by the model to be beneficial because it leads to gelation starting at the inside of the cylinder, and the temperature of the cylinder at mid-thickness would now lag behind. Early shrinkage would then cause separation, eliminating the constraint of the mandrel before significant interlaminar tensile stresses can develop within the tube.

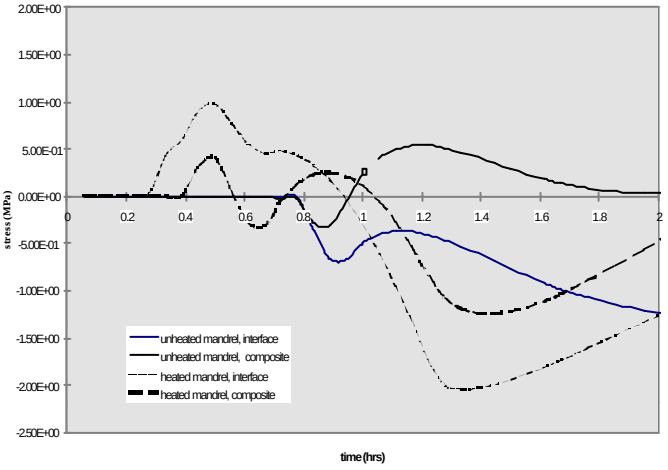

*Fig.8 Radial stress history at interface between mandrel and composite and a quarter of the way through the **50mm** composite tube*

The model was also used to predict the effect of modifying the cure cycle by using a single dwell stage to bring the whole tube to a uniform temperature closer to the gel point. This is in order to achieve more uniform curing through the thickness. Therefore in the model the dwell temperature was increased from 90° to 105°C. The second dwell at 130°C was eliminated to give greater thermal expansion early in the cure to counteract chemical shrinkage. This case was modelled with and without the heated mandrel (see Fig.8). With an unheated mandrel there is virtually no tensile stress at the interface (this was also found for the other cure cycles). The composite would not be expected to separate from the mandrel. However, inside the composite a tensile radial stress of over 0.5 MPa is generated. At this early stage in the cure and at elevated temperature, this may be enough to cause delamination failure. With the heated mandrel, a tensile radial stress at the interface is generated at an early stage, making separation of the composite from the mandrel more likely. The tensile stress is also increased by the dwell at 105°C rather than 90°C. If, for some reason (as is assumed in Figure 8) separation fails to occur during this initial phase, tensile stresses still occur in the composite, although they are lower than the unheated mandrel case.

Experimental validation of cure with heated mandrel

A special mandrel was manufactured which included oil galleries running close beneath the surface. Pumping heated oil through these channels effected mandrel heating. The component was wound onto the mandrel and placed inside a curing oven. The oven was synchronised with the oil heater, and both programmed to follow the manufacturers cure cycle. This resulted in heat being introduced to both surfaces of the component. Filament wound tubes of 20 and 50mm thickness, identical in dimensions and instrumentation to those cured by the standard method, were produced and cured using the heated mandrel.

The results showed that the temperature lag in the component during cure was reduced. For the 50mm tube the maximum temperature difference was 22°C as opposed to 36°C using the normal cure method. Most of this difference this existed across the inner 1/4 of the thickness.

Figures 9(a) and (b) show cure strains for two 50mm thick tubes, one cured normally and one on the heated mandrel. The strains recorded during cure displayed identical trends to those

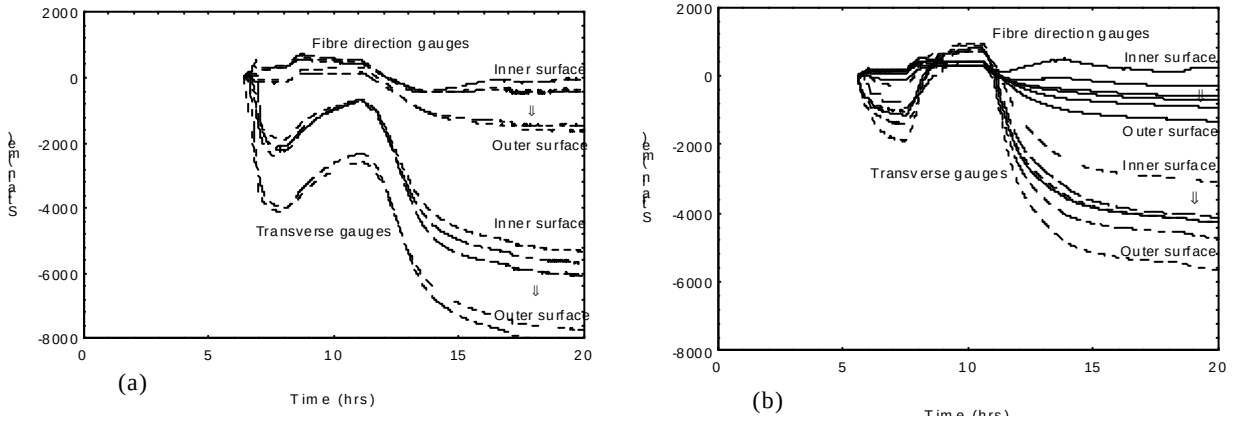

Figure 9 Strains recorded during cure of 50mm thick FW tubes (a) cured on a standard mandrel (b) cured on a heated mandrel

recorded during standard cure, but with one major difference. The compressive strain recorded shortly after gel was much smaller using the heated mandrel. This compressive strain results from shrinkage of the resin [1], and it suggests that the effect of shrinkage on the strain in the composite was much reduced with the heated mandrel.

The success of the heated mandrel in managing the residual stress was confirmed by ultrasonic C-scanning of the tube. This is represented schematically in Figure 10 which compares typical sections of 50mm thick tubes cured by the two methods. The tube cured by the conventional method of heating from the outside only, contained extensive delamination covering virtually the entire length and circumference. Curing with the heated mandrel resulted in ~85% of this tube area being free of delamination, and only contained one delamination.

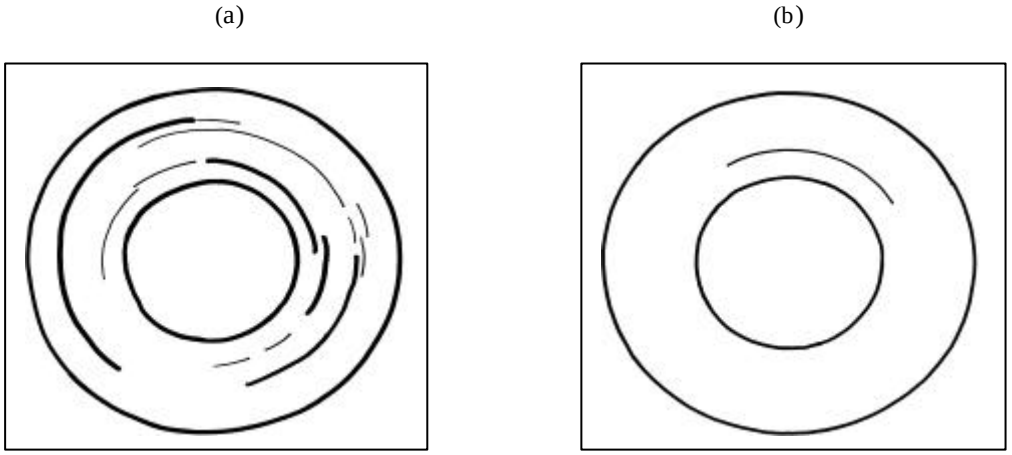

Figure 10 Delamination in 50mm thick FW tubes (a) cured on a standard mandrel (b) cured on a heated mandrel

CONCLUSIONS

1. The measurement of residual strains by embedding strain gauges during the manufacture and cure of composite tubes and panels has led to the development of a model for predicting the three-dimensional state of stress throughout the cure cycle.

2. Residual strains from embedded Bragg gratings showed very close agreement with the magnitude of final strains using electrical resistance strain gauges, and these can be used in future as a more compact less intrusive strain sensor.

3. Miniature dielectric sensors embedded in the composite provide key cure information such as time and temperature of gelation and vitrification, and the technique is being further developed to quantify the cure state at any point in the manufacturing process.

4. The 3D residual stress model is being used to predict process modifications in order to manage the residual stresses. So far it has suggested that delamination can be prevented in thick hoop wound FW tubes by curing with a heated mandrel. Experimental validation confirmed the benefits of this processing method, and delamination was virtually eliminated.

5. For a refined 3D stress model to be developed a cure kinetics model is required to allow the state of cure and resin properties to be predicted at any point in the cure cycle. This is being achieved by an iterative use of cure kinetics modelling software, experimental determination of kinetic rate constants, and Group Interaction Modelling for resin physical properties.

ACKNOWLEDGEMENTS

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