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# Residual stresses and the optimum cure cycle for an epoxy resin

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Residual stresses in carbon fibre-reinforced plastic composites arise because of the large difference in thermal expansion of the fibres and matrix. It has been suggested that these stresses might be reduced in epoxy resin matrices by curing at a lower temperature. Experiments have been made on five curing cycles, to test this possibility and to study the variations of viscosity and volume changes of the resin under different cure conditions. DSC experiments have also been made to determine the degree of cure at various stages of the cycles. It was found that a cycle with the low peak temperature of 120° C required a prohibitively long length of time to produce a complete cure. Of the other cycles studied, it is predicted that it would be advantageous, in reducing residual stresses, to use a peak temperature of 160° C, rather than 175° C, provided that a dwell of 18 min is included at 160° C to ensure a complete cure.

## 1. Introduction

The residual stresses in a fibre-reinforced plastic composite arise from the large differences in the thermal expansion properties of the fibres and matrix when the material is cooled from its fabrication temperature. In the case of an epoxy resin matrix, the situation is complicated by the volume changes that occur during the curing process, for which chemical cross-linking reactions are responsible. The net effect is always that the volume shrinkage of the matrix is much larger than that of the fibres, resulting in tensile residual stresses in the matrix. Because these stresses are capable of contributing to the initiation and growth of cracks and thereby to failure of the composite, it is desirable that they be minimized.

The volume changes occurring during the curing of a number of epoxy resins have been studied by Yates *et al.* [1]. In the present work the properties of the epoxy resin Code 87 (Cyanamid-Fothergill) were investigated. This resin has been employed as the matrix in reinforced carbon fibre composites which have been used, for example, in the construction of space craft antennae [2]. In this particular application it is known [3] that the relaxation of the residual stresses during thermal cycling in space can significantly deform an antenna, thereby leading to a degradation of its performance. One aim of the experiments reported here was to investigate different curing cycles for Code 87 resin to try to reduce the residual stresses.

It has been suggested by Chamis [4] that the residual stresses in laminates can be reduced by curing the matrix at a lower temperature, in this way reducing the mis-match in the thermal expansions of the fibres and matrix, and this possibility has been studied. From the outset it was recognized that the use of a lower temperature has two potential disadvantages. Firstly, the cure process takes longer, which increases production costs and secondly, the optimum degree of cross-linking may not be achieved.

A number of curing cycles have been considered, and during each the properties of the resin were monitored by measurements of viscosity and volume changes, and by using differential scanning calorimetry (DSC).

## 2. Cure treatments

Five different cure cycles were considered, details of which are given in Table I. Cure cycle 1 is the cycle used by British Aerospace plc in the manufacture of carbon fibre-reinforced composites for space applications. Cure cycles 2 and 3 were modified forms of cycle 1 to include dwell times which enabled the maximum viscosity of the resin to be reached, as determined from the relevant viscosity measurements. Cure cycle 4 is an alternative cycle used by British Aerospace. Cure cycle 5 was employed to study the rate of cure at a much reduced temperature.

## 3. Viscosity measurements

During the cure of an epoxy resin the viscosity increases due to the progressive cross-linking of the polymer chains. Previous work [5] indicates that gelation of the resin is immediately preceded by a rapid increase in viscosity.

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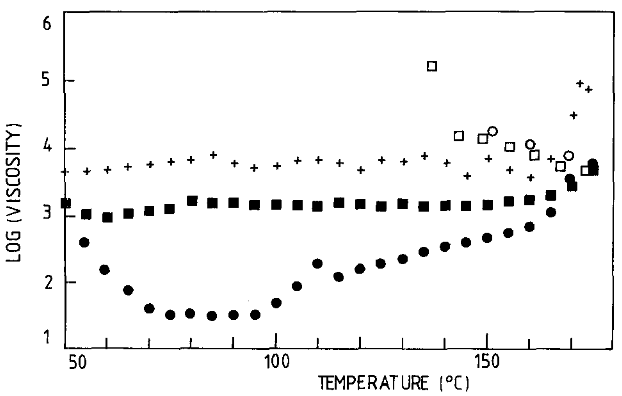

*Figure 1* Variation of viscosity (P) with temperature during cure cycle 1. (●) Run 1; (■) run 2; (+) run 3. Open symbols are for cooling.

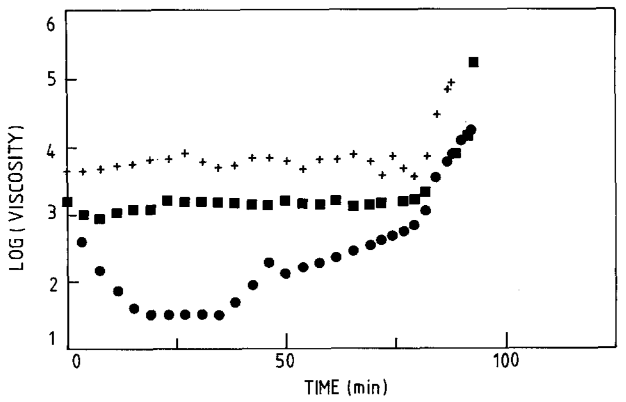

*Figure 2* Variation of viscosity (P) with time during cure cycle 1. (●) Run 1; (■) run 2; (+) run 3.

Measurements of the viscosity of Code 87 resin were made using a Ferranti-Shirley viscometer, details of which have been described previously [5]. The viscosity was determined as functions of temperature and time during cure cycles 1, 2 and 3, modified so that the starting temperature was 50° C, because at room temperature the viscosity of the resin was too high to be measurable by the apparatus. For cure cycle 1, measurements were continued into the cooling down period after the resin had reached 175° C until its viscosity approached the limits of measurement. For cure cycles 2 and 3 the resin was held at the final temperatures of 160 and 150° C, respectively, until its viscosity reached a maximum. These dwell times were subsequently incorporated into the cure cycles used for the volumetric experiments.

## 3.1. Results

Three experiments using cycle 1 were performed over a period of 2 months, using samples of resin taken randomly from two different batches. Fig. 1 shows the viscosity of the resin plotted against temperature and Fig. 2 shows the viscosity of the resin as a function of time for the same three experiments. The differences in shape of the curves were thought to be due to the ageing of the resin. In addition to the shape differences, it can be seen that the absolute value of the viscosity at any temperature increases with shelf time. The experiments were performed over a period of several weeks and, although the resin was stored in a refrigerator, some low-level cross-linking appears to have taken place. Nevertheless, in all three cases, it is clear that the rapid increase in viscosity starts at $t = 79$ min, when the temperature is 160° C and the resin is cooling from 175° C. The time taken to achieve maximum viscosity after the start of this rapid increase was 11.5 min, at which time the resin was at a temperature of 155.3° C. The average length of the entire cycle was 90.5 min.

TABLE I Curing cycles employed in the experiments

| Cycle number | Details |
|---|---|
| 1 | Raise temperature from ambient to 140° C at 1.3° C min$^{-1}$, then to 175° C at 2° C min$^{-1}$. Cool. |
| 2 | Raise temperature from ambient to 140° C at 1.3° C min$^{-1}$, then to 160° C at 2° C min$^{-1}$. Dwell for 15 min. Cool. |
| 3 | Raise temperature from ambient to 140° C at 1.3° C min$^{-1}$, then to 150° C at 2° C min$^{-1}$. Dwell for 35 min. Cool. |
| 4 | Raise temperature from ambient to 140° C at 1.3° C min$^{-1}$, then to 170° C at 2° C min$^{-1}$. Dwell for 60 min. Cool. |
| 5 | Raise temperature from ambient to 120° C at 1.3° C min$^{-1}$. Dwell until reaction is complete. Cool. |

Three similar experiments were performed using cure cycle 2. Fig. 3 shows the variation of the viscosity with time and the effects of resin ageing are again apparent. In this cure cycle the rapid increase in viscosity started after 77 min, when the temperature of the resin was 155° C, i.e. before the start of the dwell. When 160° C was reached, the resin was kept at that temperature until maximum viscosity was reached. This took an average time of 13.3 min, giving a mean overall cycle length of 92.6 min.

Results for three experiments using cycle 3 are displayed in Fig. 4. It can be seen that the viscosity started to increase rapidly after 77 min, 2.5 min into the dwell at 150° C. The average length of dwell was 28.7 min. However, a dwell time of 35 min was chosen for the volume expansion experiments, because the maximum viscosity of two specimens was reached after this time and there is a discontinuity in the curve for the third specimen at this time, suggesting that shearing had taken place. Incorporating a dwell of 35 min gives a total cycle length of 109.2 min.

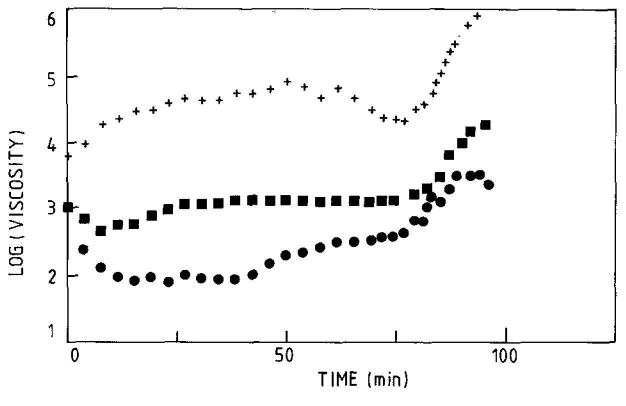

*Figure 3* Variation of viscosity (P) with time during cure cycle 2. (●) Run 1; (■) run 2; (+) run 3.

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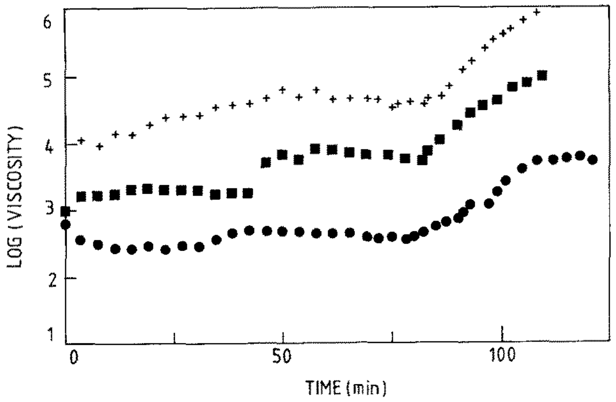

*Figure 4* Variation of viscosity (P) with time during cure cycle 3. (●) Run 1; (■) run 2; (+) run 3.

the rapid increase are compared, that for cure cycle 1 is 11.5 min, 3.8 min after 175° C is reached; for cure cycle 2, 17.1 min and cure cycle 3, 32.5 min. The rapid increase in viscosity marks the start of gelation, which was found to take longer at lower temperatures, as expected.

## 4. Volumetric measurements

The increase in cross-linking of the polymer chains also produces an overall reduction in the volume of an epoxy resin. Therefore, measuring the change in volume of a resin with respect to time and temperature during a cure cycle can indicate the rate and degree of cure at any stage of the cycle and, in particular, determine whether or not a resin is fully cured at the end of the given cycle. Hence volumetric changes were measured during all five cure cycles.

For the experiments using cure cycles 1, 2 and 3, a dilatometer with a detachable bulb, designated A, was employed. For the experiments using cure cycles 4 and 5 a second dilatometer, B, was employed in which the glass capillary tube was fused to a glass bulb partially filled with resin. The constructions of the two dilatometers are shown in Fig. 5. The dilatometers were chemically cleaned before each experiment.

For experiments using dilatometer A, the still warm resin was poured into the glass bulb, which had previously been weighed. The glass bulb was then placed in a desiccator under vacuum to remove any entrapped air. The bulb was then re-weighed; hence the weight and volume of the resin were known. The dilatometer was assembled as shown in Fig. 5, re-weighed, placed under vacuum and then silicone oil was introduced via the top of the capillary tube. The dilatometer was then weighed again so that the weight and volume of the silicone oil were known. The level of the meniscus of the silicone oil relative to a fiduciary point at the base of the capillary was noted and hence the volume of the bulb was calculated.

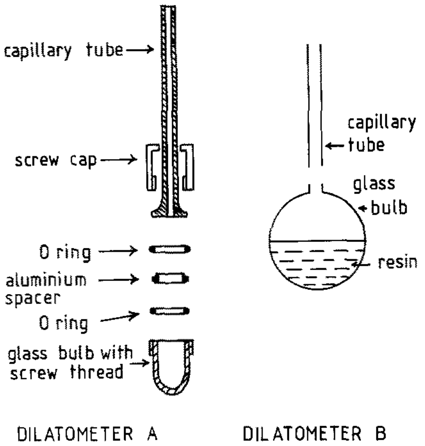

*Figure 5* Dilatometers employed; A for cure cycles 1 to 3; B for cure cycles 4 and 5.

For experiments using dilatometer B, the bulb alone was first weighed and resin was introduced via the small hole in the top. The bulb was then re-weighed. The bulb was placed under vacuum in a desiccator to remove any entrapped air. The capillary was attached to the bulb by heating the glass at the ends of each and fusing them together, whilst taking great care to keep excess heat away from the resin. The dilatometer was then weighed, placed under vacuum, and silicone oil was introduced via the top of the capillary. The level of the meniscus relative to the fiduciary point was noted. The dilatometer was then re-weighed and the volume of the bulb calculated.

For all experiments, the dilatometers were placed vertically in a constant temperature bath and taken through the relevant cure cycle. Subsequent movement of the meniscus was monitored with the aid of a cathetometer sighted through a window in the wall of the bath. The temperature of the bath was monitored using a thermocouple.

In a subsequent experiment, a dilatometer containing only silicone oil was taken through cure cycle 1. This was in order to determine the difference in temperature between the inside of the bulb and the bath fluid. These differences were then taken into consideration when calculating the temperatures of the resin. Corrections were made for the thermal expansion of the glass and silicone oil in determining the volume of the resin.

### 4.1. Results

Six experiments were performed, two using cure cycle 1, and one using each of cure cycles 2, 3, 4 and 5. The measurements were made over a period of several months, using samples of resin taken randomly from several batches.

The results of the six experiments are shown in Figs 6 to 11. In all cases a linear increase in volume is

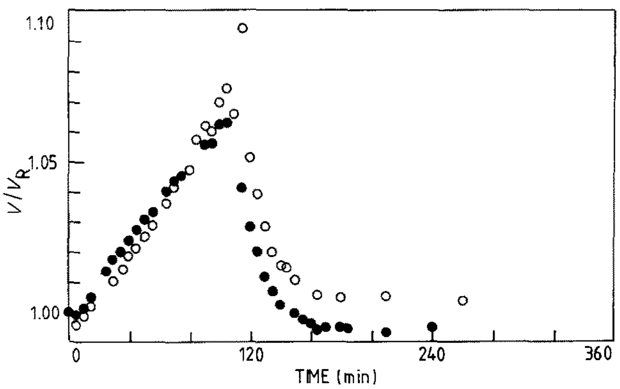

*Figure 6* Volume normalized to the initial value $V_R$ as a function of time during cure cycle 1, (●) run 1, (O) run 2.

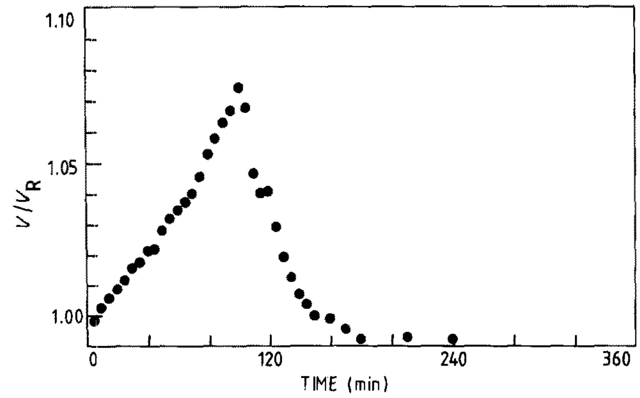

*Figure 7* Volume normalized to the initial value $V_R$ as a function of time during cure cycle 2.

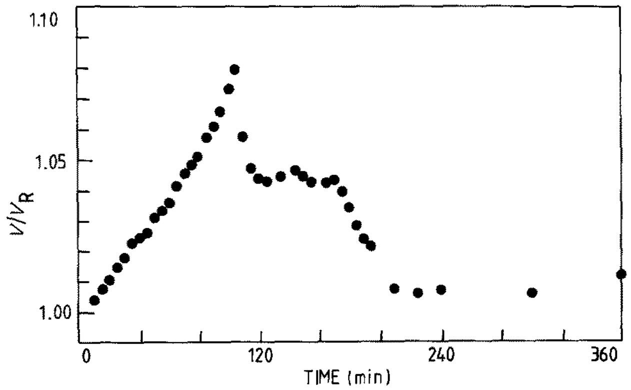

*Figure 9* Volume normalized to the initial value $V_R$ as a function of time during cure cycle 4.

observed as the temperature is increased at the start of the experiment. For cure cycles 1, 2 and 4, shrinkage appears to commence before the maximum temperature is reached. For cure cycle 3, shrinkage starts after the dwell at 150° C has started and for cure cycle 5, shrinkage starts after 85 min, approximately 10 min after the start of the dwell at 120° C.

Fig. 6 indicates that for cure cycle 1, shrinkage is very rapid at the start of the cool-down period and slows after $t$ = 120 min is reached, when the temperature of the resin is approximately 140° C. This implies that cross-linking is still taking place during this time, and that the resin is not completely cured by the time 175° C is reached. For cure cycles 2 and 3, there is no appreciable change in the gradient of the graph of volume change against time as their respective dwells end, which implies that no more cross-linking is taking place and that the resin is fully cured. Fig. 9 shows the change in volume of the resin plotted against time as it was taken through cure cycle 4. In this experiment, the resin ceases to decrease in volume very shortly after the start of the dwell, after approximately 10 min. This indicates that the resin would be fully cured at the end of a cure cycle which incorporated a dwell of this length. In the experiment using cure cycle 5, the resin shrinks much more slowly than in the other experiments. Fig. 11 shows that the rate of shrinkage slows after approximately 11 h, although some cross-linking appears to be still taking place after 98 h, indicating that the resin is still not fully cured.

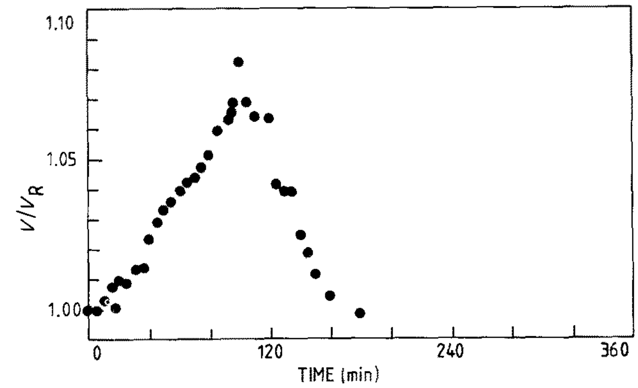

*Figure 8* Volume normalized to the initial value $V_R$ as a function of time during cure cycle 3.

## 5. Differential scanning calorimetry

In differential scanning calorimetry (DSC) the differential heat flow between a sample and a reference material is measured as a function of a linearly programmed temperature rise. For a thermosetting epoxy resin system, the plot traces the curing exotherm. Hence DSC can be used to follow and define the cure behaviour of thermosetting resins and as a quality assurance control. Carpenter [6] has described the instrumental techniques for developing epoxy cure cycles by using DSC. These techniques enable one to determine when the curing reaction starts, the period of maximum flow, gel point, period of maximum energy release and point of reaction completion for any set of time–temperature cure cycle parameters. These techniques were applied to Code 87 resin.

A Du Pont thermal analyser with a differential scanning calorimetry module was employed and runs were made at heating up rates of 5, 10 and 20° C $\text{min}^{-1}$. The resulting plots of heat flow as functions of temperature are displayed in Fig. 12. Allowing for base line variations, the exotherm peak can be characterized by four temperatures: $T_{OS}$, the onset temperature, is obtained by extrapolating the positive slope side of the curve to the base line and it is taken to indicate the start of the polymerization reaction; $T_{EXO}$ is the exotherm peak temperature; $T_{IP}$, the inflection point temperature, is approximately midway between $T_{EXO}$ and $T_{OS}$; $T_{CR}$, the temperature for completion of the cure reaction, is obtained by extrapolating the

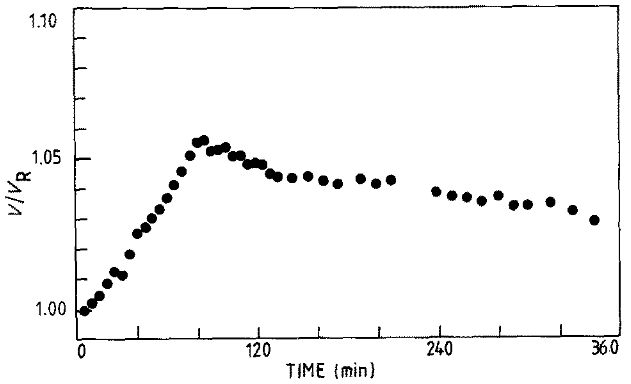

*Figure 10* Volume normalized to the initial value $V_R$ as a function of time during cure cycle 5.

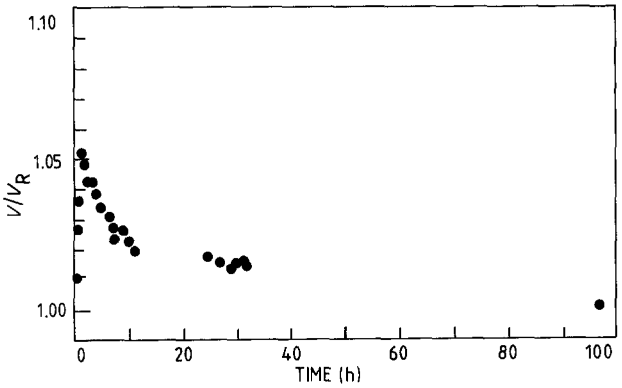

*Figure 11* Volume normalized to the initial value $V_R$ as a function of time during cure cycle 5.

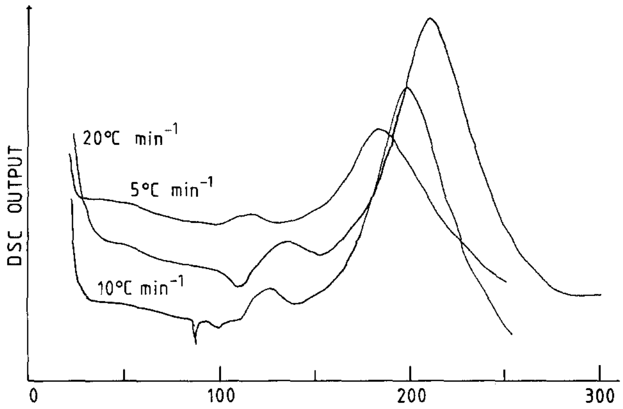

*Figure 12* DSC outputs as functions of temperature.

back side of the exotherm curve to the base line. The characteristic temperatures obtained from Fig. 12 are presented in Table II. The energy released during cure, which can be assumed to be proportional to the area under the curve, was not of interest in the present study.

## 5.1. Analysis of the DSC data

It is usually assumed [7, 8] that curing is a first-order reaction, such that the degree of cure, $x$, satisfies the equation

$$\frac{dx}{dt} = D(1 - x)e^{-A/T} \quad (1)$$

where $A$ is an activation energy and $D$ is independent of time $t$. Integrating with respect to time, and denoting by $\phi$ the uniform rate of temperature scan, $\phi = dT/dt$, the temperatures $T_{xi}$ corresponding to a certain degree of cure $x$ obtained at different heating rates $\phi_i$ are related by [8]:

$$\log \phi_i = \frac{A}{T_{xi}} + B \quad (2)$$

where $B$ is a new constant. Plotting log $\phi$ against $1/T$ for the four characteristic temperatures, it was found that both $A$ and $B$ were weakly dependent on $x$, as indicated in Table II.

Following Carpenter [6], it is supposed that the curing of the resin under isothermal conditions can be described by the relationship

$$t_x = C_x T^2 10^{-A/T} \quad (3)$$

where $t_x$ is the time to reach a specified degree of cure $x$, and $C_x$ is a constant for given $x$. It is implicitly assumed that the activation energy $A$ can be derived from a series of temperature scans employing Equation 2. A linear heat-up rate can be considered to comprise a series of isothermal steps, each of duration time $\delta t$, over a range from room temperature, $T_R$ to the temperature at which the required degree of cure is reached. For a given $\phi_i$, the condition

$$\frac{1}{\phi_i}\sum_{T=T_R}^{T_{xi}} \frac{\delta t}{t_x(T)} = 1 \quad (4)$$

must be satisfied, which determines the values of $C_x$. It was found that the $C_x$ obtained, displayed in Table II, were independent of $\phi_i$.

## 5.2. Times to gel point and complete cure

Temperatures $T_{IP}$ are identified with the gel point of the Code 87 resin. For cure cycles 1 to 4, described in Table I, the above analysis predicts that gelation takes place when the resin reaches a temperature $T_G$ given by

$$\frac{1}{\phi_1}\sum_{293}^{413}\frac{1}{t_{IP}} + \frac{1}{\phi_2}\sum_{413}^{T_G}\frac{1}{t_{IP}} = 1 \quad (5)$$

where $t_{IP}$ is given by Equation 3, with appropriate constants from Table II, and $\phi_1 = 1.3\,\mathrm{K\,min^{-1}}$ and $\phi_2 = 2.0\,\mathrm{K\,min^{-1}}$. Solution of Equation 5 gave $T_G = 416\,\mathrm{K}$, reached after a time of 98 min.

In the case of cure cycle 5, gelation was predicted to occur during the dwell at 393 K. Under isothermal conditions at 393 K, Equation 3 indicates that the gel point is reached after 49 min. In cure cycle 5 the dwell is preceded by heating at the constant rate $\phi_1$, and hence the time into the dwell $t_D$ at which gelation takes place is given by

$$t_D = 49\left(1 - \frac{1}{\phi_1}\sum_{293}^{393}\frac{1}{t_{IP}}\right) \quad (6)$$

It was found that $t_D = 37$ min and the total time taken from commencing the cycle was 129 min.

Similar calculations were made to estimate the degree of cure when the final temperatures of each

TABLE II Characteristic temperatures determined from DSC scans and parameters A, B and C deduced from analysis of DSC data

| | | $T_{OS}$ (K) | $T_{IP}$ (K) | $T_{EXO}$ (K) | $T_{CR}$ (K) |
|---|---|---|---|---|---|
| Heating rate (K min$^{-1}$): | 5 | 420.0 | 438.3 | 456.5 | 504.5 |
| | 10 | 433.0 | 452.3 | 471.5 | 513.0 |
| | 20 | 446.0 | 465.0 | 484.0 | 532.3 |
| $A$ (K) | | −4336 | −4609 | −4800 | −5577 |
| $B$ | | 11.0 | 11.2 | 11.2 | 11.8 |
| $C$ ($\times 10^{-15}$) | | 1.0201 | 0.5910 | 0.6022 | 0.1299 |

TABLE III Predictions from the DSC analysis for the five cure cycles

| Cure cycle | Degree of cure, $x$ (%) | Dwell required to complete cure (min) |
|---|---|---|
| 1 | 12.5 | 6.4 |
| 2 | 4.7 | 17.6 |
| 3 | 2.6 | 34.5 |
| 4 | 8.7 | 9.0 |
| 5 | 0.3 | 3100.0 |

cycle were reached. The duration of a dwell at these temperatures, that would be needed to complete the cure, was also determined. The results obtained are presented in Table III.

## 6. Discussion

The two events in the cure cycle of Code 87 resin that were of most interest are the gel point and the point of complete cure. The viscosity experiments indicated that gel took place after a mean time of 78 min, when the temperature of the resin was 157° C, i.e. after the start of the dwell for cure cycle 3. This is corroborated by the volume expansion measurements, in which shrinkage started before the dwell in the experiment using cure cycle 2, and after it for that using cure cycle 3. However, the DSC calculations suggest that gelation takes place at a temperature of 143° C for cure cycles 1, 2, 3 and 4. The reason for this is that DSC is a much more sensitive method than the other two, and can detect much lower levels of cross-linking. For cure cycle 5, the volume expansion result suggests that gelation starts 10 min into the dwell at 120° C, whereas the DSC calculation indicates 37 min. Unfortunately, there is no viscosity result for this cure cycle.

The viscosity experiments performed using cure cycle 1 suggest that the resin is not fully cured by the time it reaches the final temperature of 175° C; maximum viscosity is not attained until 3.8 min after this time. The volume expansion experiments confirmed this conclusion, because the resin continued to shrink during the cooling-down period, for approximately 12.5 min. The DSC calculations suggested that cure would be completed by a dwell of 6.4 min at 175° C, a time closer to that of the volume expansion result than the viscosity result.

The results of the viscosity measurements led to dwells of 13.3 and 35 min being incorporated into cure cycles 2 and 3, respectively. The volume expansion results showed that the resin was indeed fully cured at the end of both cure cycles. The DSC calculations suggested dwell times of 17.6 and 34.5 min, which tie in very well with the other two results. Both the volume expansion experiments and the DSC calculations indicated that a dwell of 1 h at 170° C in cure cycle 4 was unnecessary, and they suggested that a dwell of 10 min would be sufficient.

For cure cycle 5, the volume expansion and DSC results disagree. DSC suggested that cure is completed 51.6 h into the dwell at 120° C, whereas the volume expansion experiments implied that cure was still not complete after 98 h. However, given the uncertainties in the volumetric measurements over such long periods, and the expected errors in the DSC calculated values, these differences may not be significant. It is clear that cycle 5 is too long to be of practical use.

For cycles 1 to 4 the predicted times required for complete cure differ very little from one another. In view of the benefit gained in reducing built-in thermal stresses by curing at a lower temperature, it is proposed that cure cycle 2 offers a significant advantage over the other cycles studied. The fractional reduction in residual stress, $\sigma$, in a unidirectional fibre-reinforced resin, resulting from using the lower curing temperature of 160° C, can be estimated from the expression

$$\Delta\sigma/\sigma = \int_{443}^{448} [\alpha_{\mathrm{m}}(T) - \alpha_{\|\mathrm{f}}]\,\mathrm{d}T \Big/ \int_{300}^{448} [\alpha_{\mathrm{m}}(T) - \alpha_{\|\mathrm{f}}]\,\mathrm{d}T \tag{7}$$

where $\alpha_{\|\mathrm{f}}$ is the expansion coefficient of the fibres. Assuming carbon fibres, then $\alpha_{\|\mathrm{f}}$ is very much less than the thermal expansion coefficient of the matrix, $\alpha_{\mathrm{m}}$, and it can be set approximately to zero. The temperature variation of the resin expansion coefficient was not measured, but it can be estimated from the work of Yates *et al.* [9] on similar resin systems. The results for the latter suggest that

$$\alpha_{\mathrm{m}}(T) \simeq [4.39 + 0.018(T - 300)] \times 10^{-5}\,\mathrm{K}^{-1} \tag{8}$$

between 300 and 448 K. Employing this expression for $\alpha_{\mathrm{m}}$ in Equation 7 gives an estimated decrease in residual stress of 12%, which is a very worthwhile reduction.

## 7. Conclusions

Results are presented for the variations in viscosity and volume of Code 87 resin as it is taken through five different cure cycles. DSC data have also been obtained for the resin and they have been analysed to predict the variation of the degree of cure throughout the five cycles considered.

DSC analysis indicated that the first cross-linking during a cure cycle occurs at a temperature of 143° C, but rapid cross-linking, as manifest in rapid viscosity and volume changes, does not commence until the temperature reaches 157° C.

It was found that for all five cycles considered, the cure was not complete when the resin just reached the maximum temperature in a cycle. The times of dwells at these temperatures required to produce complete cure were predicted from the DSC analysis and were found to range from 6 min at 175° C to 35 min at 150° C. For a low-temperature cure cycle with a maximum temperature of 120° C, the predicted dwell time was found to be prohibitively long, in excess of 50 h.

It was concluded that reducing the peak temperature from 175 to 160° C could result in a cycle which produced a fully cured resin with hardly any increase in processing time. At the same time, because of the lower temperature, there should be a significant reduction in residual stresses in the final composite components.

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