

Viscoelastic analysis of residual stresses in a unidirectional laminate

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Abstract. The residual stress distribution in a unidirectional graphite/epoxy laminate induced during the fabrication process is investigated at the microstress level within the scope of linear viscoelasticity. To estimate the residual stresses, the fabrication process is divided into polymerization phase and cool-down phase, and strength of materials approach is employed. Large residual stresses are not generated during polymerization phase because the relaxation modulus is relatively small due to the relaxation ability at this temperature level. The residual stresses increase remarkably during cool-down process. The magnitude of final residual stress is about 80% of the ultimate strength of the matrix material at room temperature. This suggests that the residual stress can have a significant effect on the performance of composite structure.

Key words: residual stress; unidirectional laminate; fiber; matrix; viscoelasticity; polymerization phase; cool-down phase.

1. Introduction

Residual stresses in composite laminates are an unavoidable consequence of the volumetric shrinkage in cross-linking resins during polymerization and the difference in coefficients of thermal expansion between fibers and polymeric matrices. Such residual stresses may cause distortion of finished components and premature failure upon tensile loading.

A typical autoclave curing process of graphite/epoxy composites is shown in Fig. 1. Details of an autoclave curing process of thermosetting composites can be found in Slobodzinski (1984) and Tsai and Hahn (1980); however, a brief review of such process is in order. The laminate is put in a vacuum bag to squeeze out the entrapped air and is slowly heated in an autoclave. A pressure in the range of 80~100 psi is applied to drive out volatile matter at around 135°C, then a temperature of 160~180°C is maintained for 1~2 hours to finish the polymerization. The temperature is then cooled from the cure temperature to the room temperature and the cured laminate is removed from the autoclave.

During the polymerization process (A-B region in Fig. 1), the matrix shrinks due to chemical reaction, i.e. cross-linking of material. The deformation of the matrix is constrained by the fibers, and hence residual stresses are built up in each ply. The mismatch in thermoelastic properties between fiber and matrix results in significant thermal stresses upon cool down from the processing temperature. Such stresses result from the matrix having a higher thermal coefficient

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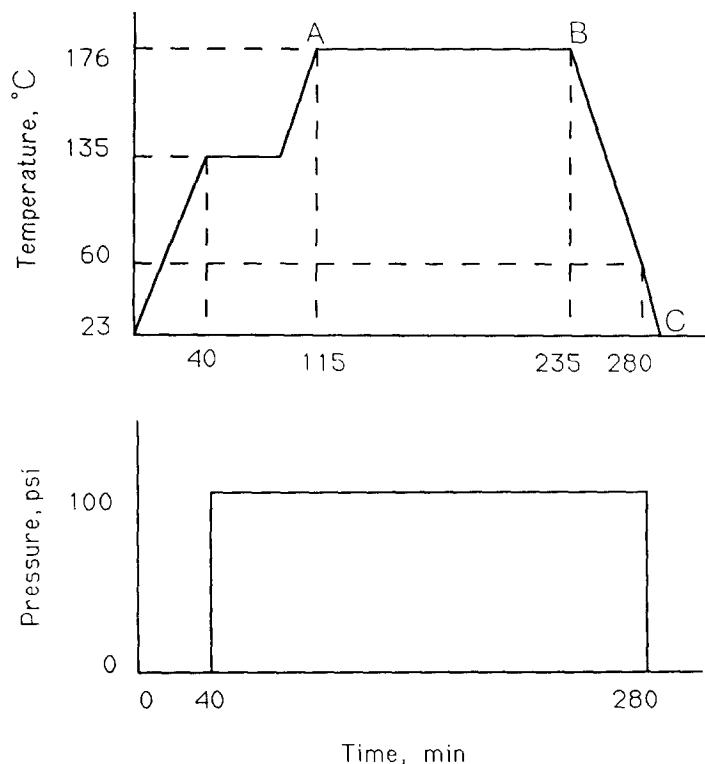


Fig. 1 Typical cure procedure of graphite/epoxy composite.

of expansion than the fibers. These residual stresses can play a very important role during subsequent loading of the composite system.

Residual stresses in fiber composites have received much attention. A linear elastic stress analysis shows that the thermal residual stresses may be large enough to cause ply failure in the absence of applied external stress or premature failure upon external loading (Hahn and Pagano 1975, Hahn 1976, and Kim and Hahn 1979). The assumption of linear elastic behavior, however, tends to overestimate the residual stresses by ignoring the time and temperature dependence of the resin's response. Residual stresses may be reduced by changing the cool-down path in a cure cycle because the resin is inherently viscoelastic (Roy and Murthy 1976, Weitsman and Ford 1977, and Weitsman 1979).

In this paper, an analysis of residual microstresses in a unidirectional graphite/epoxy laminate induced during fabrication process is performed by using viscoelastic model for matrix resin. A unidirectional laminate is usually not used in structural components due to the low strength in the transverse direction. In order to be optimal for all external loading conditions, a multidirectional laminate is employed in structural application. A detailed investigation of a unidirectional laminate problem is the first step to solving the more complex problem of a multidirectional laminate. To estimate the residual stresses, the fabrication process is divided into polymerization phase and cool-down phase. Solution of a simple model of a unidirectional laminate leads to a Volterra integral equation of the second kind. The numerical solution of this integral equation describes the residual stress state generated in a unidirectional laminate during polymerization and cool-down phases.

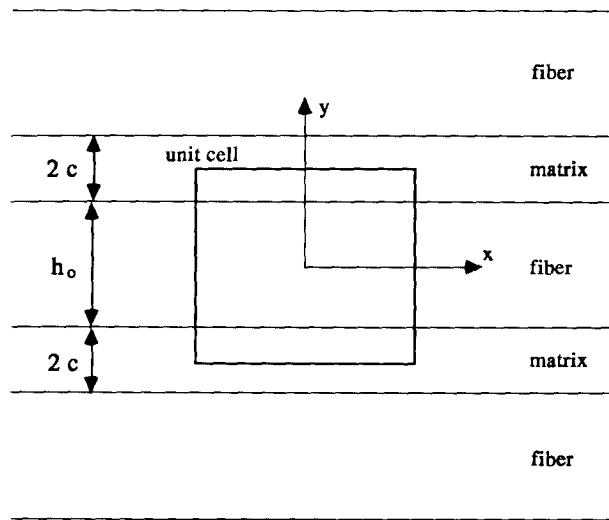


Fig. 2 Idealized model.

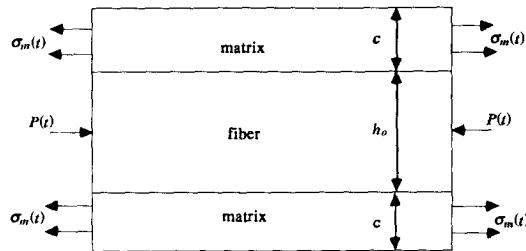


Fig. 3 Built-up of residual stresses during cure.

2. Analytical model

A unidirectional laminate, idealized as an infinite layered solid, is shown schematically in Fig. 2. The fibers are assumed to be straight. In the present work, a strength of materials approach is employed to estimate the residual stresses in a unidirectionally reinforced composite.

To simplify the problem, the following additional assumptions are made:

- The fiber-matrix bond is perfect.
- The fiber is linearly elastic while the matrix is linearly viscoelastic.
- Point A in Fig. 1 is taken as the stress-free state because the epoxy is viscous enough at that point to allow complete relaxation of any initial residual stresses.
- Complete polymerization takes place in region A-B in Fig. 1 and chemical reaction during polymerization occurs uniformly throughout the epoxy resin.
- A uniform temperature change exists in the unit cell during cool-down (see Fig. 2).
- Since the thickness of the fiber and the matrix is very small compared to its other dimensions, all quantities are assumed to be constant over the fiber and the matrix thickness. The influence of Poisson's ratio is neglected.
- The interaction between adjacent fibers is neglected.

3. Governing equations

3.1. Polymerization stress

As the matrix is a homogeneous and isotropic viscoelastic solid, the constitutive law (without ageing effect) in integral form for the one-dimensional problem as shown in Fig. 3 can be expressed as follows:

$$\sigma_m(t) = \int_{-\infty}^t Y_m(t-t') \frac{\partial \varepsilon_m(t')}{\partial t'} dt' \quad (1)$$

where $\sigma_m(t)$ is the stress, $\varepsilon_m(t)$ is the strain, and $Y_m(t-t')$ is the relaxation modulus.

During polymerization of thermosetting resins, large changes in the mechanical properties occur. In order to include these changes in the calculation of the polymerization stresses consider the polymerization phase to be equivalent to an ageing process. To this end, an ageing parameter is introduced leading to a new constitutive equation as follows:

$$\sigma_m(t) = \int_{-\infty}^t Y_m(t-t', t) \frac{\partial \varepsilon_m(t')}{\partial t'} dt' \quad (2)$$

Comparing Eq. (2) with Eq. (1), the second variable t in $Y_m(t-t', t)$ represents the ageing effect of the matrix during polymerization.

During polymerization phase, the length of the element changes in the longitudinal direction. In view of the small fiber thickness and matrix thickness compared to its other dimensions in a unidirectional laminate it is assumed that the change in length occurs uniformly across the element. The compatibility condition requires

$$\varepsilon'_m(t) = \varepsilon'_f(t) \quad (3)$$

where ε'_m and ε'_f are the total longitudinal strains in the matrix and the fiber, respectively.

The total longitudinal strain in the matrix, ε'_m , is given by

$$\varepsilon'_m(t) = \varepsilon_c(t) + \varepsilon_m(t) \quad (4)$$

where ε_c is the strain in the longitudinal direction due to chemical shrinkage of the matrix resin and ε_m is the strain in the longitudinal direction due to the residual stress in the matrix.

The longitudinal strain in the fiber is given by (see Fig. 3)

$$\varepsilon'_f(t) = -\frac{P(t)}{h_0 E_f} \quad (5)$$

where $P(t)$ is the longitudinal force per unit length induced during polymerization, h_0 is the thickness of the fiber, and E_f is the Young's modulus of the fiber.

From Eqs. (4) and (5), Eq.(3) becomes

$$\varepsilon_m(t) = -\varepsilon_c(t) - \frac{P(t)}{h_0 E_f} \quad (6)$$

The equilibrium relation in the longitudinal direction in Fig. 3 is given by

$$P(t) = 2c\sigma_m(t) \quad (7)$$

where $2c$ is the thickness of the matrix. Substituting Eqs. (6) and (7) into Eq. (2) and integrating by parts, the following Volterra integral equation of the second kind is obtained.

$$\begin{aligned} \sigma_m(t) & \left[1 + \frac{2c Y_m(0, t)}{h_0 E_f} \right] \\ & = - \int_0^t Y_m(t-t', t) \frac{\partial \epsilon_c(t')}{\partial t'} dt' + \frac{2c}{h_0 E_f} \int_0^t \sigma_m(t') \frac{\partial Y_m(t-t', t)}{\partial t'} dt' \end{aligned} \quad (8)$$

The form of the resulting equation may be simplified by introducing the following dimensionless variables:

$$\begin{aligned} \beta &= \frac{h_0}{2c}, \quad d = \frac{E_f}{Y^*}, \\ \tilde{Y}_m(t-t', t) &= \frac{Y_m(t-t', t)}{Y^*}, \quad \tilde{\sigma}_m(t) = \frac{\sigma_m(t)}{Y^*} \end{aligned} \quad (9)$$

where Y^* is glassy modulus of the matrix at room temperature. Then, Eq. (8) becomes

$$\begin{aligned} & \tilde{\sigma}_m(t) [1 + \lambda \tilde{Y}_m(0, t)] \\ & = \int_0^t \tilde{Y}_m(t-t', t) R(t') dt' + \lambda \int_0^t \tilde{\sigma}_m(t') \bar{K}_c(t, t') dt' \end{aligned} \quad (10)$$

where $\lambda = \frac{1}{d\beta}$, $R(t) = -\frac{\partial \epsilon_c(t)}{\partial t}$, and $\bar{K}_c(t, t') = \frac{\partial \tilde{Y}_m(t-t', t)}{\partial t'}$

3.2. Thermal stresses during cool down

During cooling down to room temperature (region B-C in Fig. 1), additional residual stresses develop due to differential thermal expansion of the constituent materials. The structural response of viscoelastic medium is affected by temperature mainly through thermal expansion and changes in the relaxation time and the retardation time: these time constants are normally very sensitive to temperature. The matrix behavior can be characterized in this case by a 'thermo-rheologically simple' material; i.e. the effect of temperature on relaxation modulus is accounted for by a corresponding horizontal shift when the modulus is plotted against logarithmic time scale. The real time in the relaxation modulus function is replaced by a time-temperature parameter called reduced time, ξ , given by

$$\xi = F(t) = \int_0^t \frac{d\alpha'}{a_T[T(\alpha')]} \quad (11)$$

where $a_T[T(\alpha')]$ is the shift factor, a function of temperature history.

For the epoxy used in composite systems, Weitsman (1979) proposed the dependence of a_T on the temperature as follows:

$$a_T = \exp \left[\frac{6480}{T(t)} - 21.82 \right] \quad (12)$$

where the time t is in minutes, and the temperature T is in degrees in Kelvin.

During cool-down of the fiber composite, the changes of mechanical properties are very large and the thermo-rheologically simple representation is not completely adequate. For this reason, it is necessary to include the temperature effect on the mechanical properties. The constitutive equation with such an effect can be expressed as follows:

$$\sigma_m(t) = \sigma_{mB} + \int_0^t Y_m^T[\xi - \xi', T(t)] \frac{\partial \varepsilon_m^T(t')}{\partial t'} dt' \quad (13)$$

where σ_{mB} is the axial stress in the matrix at point B in Fig. 1, Y_m^T is the relaxation modulus during cool-down, ε_m^T is the longitudinal strain due to the residual stress during cool-down, and ξ and ξ' are given by

$$\xi = F(t), \quad \xi' = F(t') \quad (14)$$

The $T(t)$ in $Y_m^T[\xi - \xi', T(t)]$ represents the temperature effect upon the mechanical properties during cool-down.

The longitudinal strain due to the residual stress during cooling down in the matrix, $\varepsilon_m^T(t)$, is given by the expression

$$\varepsilon_m^T(t) = -\frac{P(t) - P_B}{h_0 E_f} + \alpha_f \Delta T(t) - \alpha_0 \Theta(t) \quad (15)$$

where P_B is the axial force per unit length in the fiber at the end of polymerization (point B in Fig. 1), α_f is the coefficient of thermal expansion of the fiber, and the 'pseudo-temperature' $\Theta(t)$ and α_0 are defined by

$$\begin{aligned} \Theta(t) &= \frac{1}{\alpha_0} \int_{T_0}^{T(t)} \alpha_m(T') dT', \\ \alpha_0 &= \alpha_m(T_0) \end{aligned} \quad (16)$$

Here $\alpha_m(T)$ is the temperature-dependent coefficient of thermal expansion of the matrix and α_0 value at the base temperature T_0 . If, in particular, $\alpha_m(T)$ is constant, Eq. (16) becomes

$$\begin{aligned} \alpha_m(T) &= \alpha_0 \\ \Theta(t) &= T(t) - T_0 = \Delta T(t) \end{aligned} \quad (17)$$

Through a procedure similar to that in the previous section, one obtains the following Volterra integral equation of the second kind from Eqs. (13) and (15),

$$\begin{aligned} &[\tilde{\sigma}_m(t) - \tilde{\sigma}_{mB}] \{1 + \lambda \tilde{Y}_m^T[0, T(t)]\} \\ &= \int_0^t \tilde{Y}_m^T[\xi - \xi', T(t)] A(t') dt' + \lambda \int_0^t [\tilde{\sigma}_m(t') - \tilde{\sigma}_{mB}] \bar{K}_T[\xi - \xi', T(t)] dt' \end{aligned} \quad (18)$$

where $\lambda = \frac{1}{d\beta}$, $\bar{K}_T[\xi, \xi', T(t)] = \frac{\partial \tilde{Y}_m^T[\xi - \xi', T(t)]}{\partial t'}$, and

$$A(t') = \frac{\partial}{\partial t'} [-\alpha_0 \Theta(t') + \alpha_f \Delta T(t')].$$

4. Calculation procedure and material properties

4.1. Polymerization stress

Eq. (10) is in a convenient form for numerical step-by-step integration. By using the trapezoidal rule, Eq. (10) is changed into a set of algebraic equations. Eq. (10) can be rewritten for constant

stepsize $h > 0$ in the following form

$$\begin{aligned} & \tilde{\sigma}_m(nh) \\ &= \frac{h}{2D} \left[\tilde{Y}_m(nh, nh) R(0) + 2 \sum_{m=1}^{n-1} \tilde{Y}_m(nh - mh, nh) R(mh) + \tilde{Y}_m(0, nh) R(nh) \right] \\ &+ \frac{\lambda h}{2D} \left[\tilde{\sigma}_m(0) \bar{K}_c(nh, 0) + 2 \sum_{m=1}^{n-1} \tilde{\sigma}_m(mh) \bar{K}_c(nh, mh) \right] \quad (n=1, 2, 3, \dots) \end{aligned} \quad (19)$$

assuming the denominator, $D = 1 + \lambda \tilde{Y}_m(0, nh) - \frac{\lambda h}{2} \bar{K}_c(nh, nh)$, does not vanish.

The initial value of $\tilde{\sigma}_m$ is given by

$$\tilde{\sigma}_m(0) = 0 \quad (20)$$

Taking $n=1, 2, 3, \dots$ in Eq. (19) successively gives equations for evaluation of $\tilde{\sigma}_m(h)$, $\tilde{\sigma}_m(2h)$, $\tilde{\sigma}_m(3h)$, \dots , respectively, each equation determining the next value of $\tilde{\sigma}_m$ in terms of values already obtained.

Several parameters affect the residual stresses in a unidirectional composite: fiber volume fraction, rate of chemical shrinkage, relaxation time, ageing properties, and cooling rate. Unfortunately, there is not enough data on the thermosetting type of polymer which would be sufficient to permit the precise evaluation of the polymerization stresses.

In the present work, the three element model is selected to represent the behavior of the matrix material during polymerization as follows:

$$Y_m(t-t', t) = E_0(t) + E_1(t) \exp\left[-\frac{t-t'}{\alpha^*(t)}\right] \quad (21)$$

where $\alpha^*(t)$ is the relaxation time. If E_0 , E_1 , and α^* are given, the numerical solution for polymerization stress follows.

According to Zweben (1984), the Young's modulus of epoxy matrix at 176°C (60% relative humidity) is about 108.75 ksi. This value can be regarded as the glassy modulus of epoxy matrix at the end of polymerization (point B in Fig. 1). Taratorin, *et al.* (1970) conducted an experimental study to determine the relaxation modulus of epoxy material at temperature from 102°C to 116°C. Through stress relaxation tests, they have shown that the cured epoxy resin has an equilibrium modulus $E_0 = 3.588$ ksi and a relatively narrow spectrum of relaxation time. For example, a minimum relaxation time of $\alpha_{min}^* = 1.781 \times 10^2$ (sec) and a maximum relaxation time of $\alpha_{max}^* = 1.781 \times 10^5$ (sec) have been obtained at 102°C. Roy and Murphy (1976) have used 10^4 (min) as a representative relaxation time in the computation of residual stresses during cooling from 75°C to 25°C. Lee, *et al.* (1982) performed the experiment to measure the viscosity of epoxy resin as a function of time. Since the relaxation time is proportional to the viscosity of the resin, their experimental result is useful in estimating the change of relaxation time during polymerization.

Using the information just described, the following estimates of the material properties are made:

$$E_0(0) = 0,$$

$$E_1(0) = 8.7 \text{ psi},$$

$$E_0(t_B) = 2.175 \times 10^4 \text{ psi},$$

$$\begin{aligned} E_o(t_B) + E_{\text{v}}(t_B) &= 1.088 \times 10^5 \text{ psi,} \\ \alpha^*(0) &= 100 \text{ sec, } \alpha^*(t_B) = 10^4 \text{ sec} \end{aligned} \quad (22)$$

When the composite is being cured, the viscoelastic nature of the matrix affects the polymerization stress field caused by chemical shrinkage, along with the time rate of change of material properties and shrinkage. Three types of matrix behavior during polymerization are considered here. First, a total chemical shrinkage $\epsilon_c = -0.010$ in/in is used. In type 1, the matrix shrinkage and the change of material properties are taken to be linearly proportional to time t . In type 2, the shrinkage and the change of material properties are assumed to be proportional t^2 , and in type 3, they are proportional to \sqrt{t} .

In order to complete the numerical calculation, the following material properties have been used (Bikales 1967):

$$\begin{aligned} E_f &= 3.25 \times 10^7 \text{ psi} \\ h_o &= 3.15 \times 10^{-4} \text{ inches} \\ \beta &= 1.222 \\ V_f(\text{fiber volume fraction}) &= 0.55 \end{aligned} \quad (23)$$

4.2. Thermal stress

The longitudinal thermal stress in the matrix during cool-down can be calculated from Eq. (18) using the fact that the initial value of $\tilde{\sigma}_m$ is $\tilde{\sigma}_{mB}$. The next steps are the same as those used in evaluating the polymerization stress. To obtain the thermal stress, a suitable expression for the relaxation modulus during cool-down is needed. Weitsman (1979) has proposed that the relaxation modulus during cool-down be given by

$$Y_m^T(\xi) = \frac{4.64 \times 10^5}{[1 + 0.0336\xi^{0.19}]} \text{ psi} \quad (24)$$

However, as shown in Zweben (1984) and Miyano, *et al.* (1986), the change of material properties due to temperature drop is very large. Therefore, it is necessary to include the effect of temperature change upon the mechanical properties.

In this study, the following modified relaxation modulus is employed

$$Y_m^T(\xi) = \frac{4.64 \times 10^5 g(T)}{[1 + 0.0336\xi^{0.19}]} \text{ psi} \quad (25)$$

Using data of Zweben (1984) and assuming $g(T)$ is a linear function of T , the relaxation modulus during cool-down becomes

$$Y_m^T(\xi) = \frac{4.64 \times 10^5 (2.28 - 0.00433 T)}{[1 + 0.0336\xi^{0.19}]} \text{ psi} \quad (26)$$

where T is the absolute temperature.

Other material properties used are as follows (Shimbo, *et al.* 1981):

$$\begin{aligned} \alpha_m &= 1.8 \times 10^{-4}/^\circ\text{C in/in } (T > T_g) \\ &= 0.6 \times 10^{-4}/^\circ\text{C in/in } (T < T_g) \\ \alpha_f &= -1.0 \times 10^{-6}/^\circ\text{C in/in} \end{aligned} \quad (27)$$

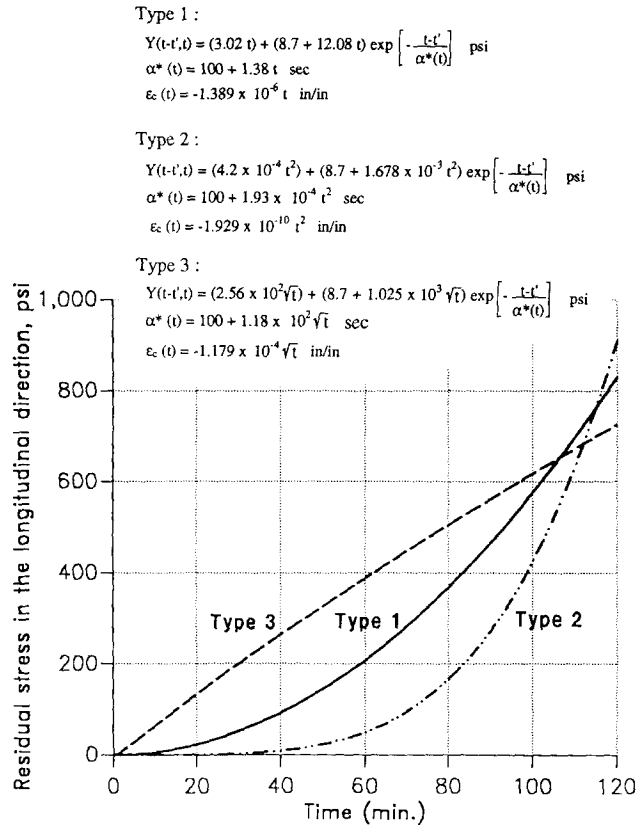


Fig. 4 Residual stresses in the matrix induced during polymerization process.

where T_g (glass transition temperature) is 388°K.

5. Discussion and conclusions

Fig. 4 shows the polymerization stresses calculated for each type of matrix behavior. The polymerization stresses depend significantly on the matrix behavior during polymerization, but the difference in the final stresses corresponding to each of assumed material response is less than 180 psi, which is relatively small. The polymerization stress of the matrix (type 1) at the end of polymerization is 0.830×10^3 psi which is about 25% of the ultimate strength of the matrix at 176°C. (The ultimate strength of epoxy matrix at 176°C is about 0.33×10^4 psi.)

The residual stress during cool-down increase remarkably as shown in Fig. 5. The polymerization stress shown in Fig. 5 has been obtained using the matrix model type 1. The final residual stress is 0.59×10^4 psi, which is 79% of the ultimate strength of the matrix at room temperature. (The ultimate strength of matrix at room temperature is 0.75×10^4 psi.) This suggests that the resulting residual stresses can have a significant effect on the performance of composite structures by initiating matrix crack, local debonding at poor bonding regions of the fiber-matrix interface, or causing premature matrix failure under external loading.

Based on the numerical results obtained, it is concluded that the major cause of the development

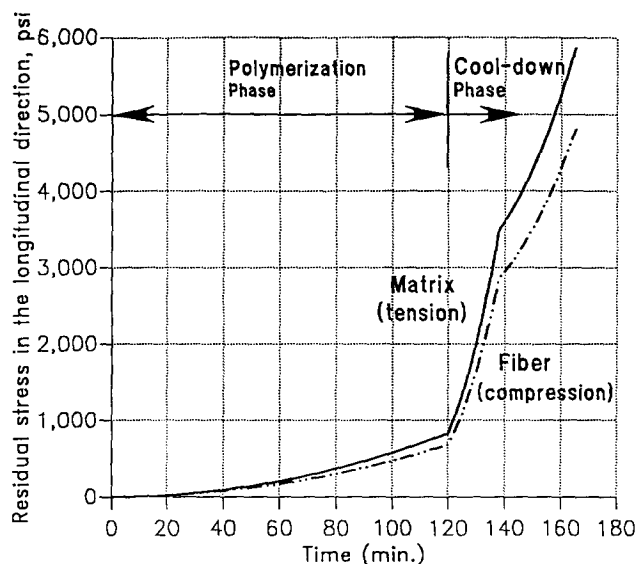


Fig. 5 Residual stresses in the matrix induced during fabrication process.

of residual stresses is the temperature difference coupled with the large thermal expansion mismatch between the fiber and matrix. Therefore, long annealing of these residual stresses through a postcure at the cure temperature is not effective. The thermal residual stresses can be reduced by changing the cool-down history because the matrix resin is inherently viscoelastic. Consequently, a study of the effect of process history on the residual stress can be recommended as further work in the future.

This work represents the first step toward achieving the goal of having a reliable method for evaluating the residual stress state and its effect on the performance of a final product. In this study, a graphite/epoxy composite material has been selected as being a technical interest. This method, however, can be extended to other types of composite materials based on polymeric matrices. As mentioned earlier, the computation conducted in the present research is based upon incomplete curing data. Should new data on the material properties for polymerization phase become available, the calculation can be readily modified.

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