(2)

TECHNICAL REPORT BRL-TR-3380

BRL

INFLUENCE OF CURE SHRINKAGE ON PROCESS-INDUCED STRESS AND DEFORMATION IN THICK THERMOSETTING COMPOSITES

TRAVIS A. BOGETTI
U.S. ARMY BALLISTIC RESEARCH LABORATORY

JOHN W. GILLESPIE, JR.
UNIVERSITY OF DELAWARE

JULY 1992

U.S. ARMY LABORATORY COMMAND

BALLISTIC RESEARCH LABORATORY
ABERDEEN PROVING GROUND, MARYLAND

NOTICES

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE July 1992

3. REPORT TYPE AND DATES COVERED Final, Jun 89–Jul 91

4. TITLE AND SUBTITLE
Influence of Cure Shrinkage on Process-Induced Stress and Deformation in Thick Thermosetting Composites

5. FUNDING NUMBERS
PR: 1L162618AH80

6. AUTHOR(S)
Travis A. Bogetti and John W. Gillespie, Jr.*

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U.S. Army Ballistic Research Laboratory
ATTN: SLCBR-DD-T
Aberdeen Proving Ground, MD 21005-5066

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
BRL–TR–3380

11. SUPPLEMENTARY NOTES
*John W. Gillespie is the Associate Director for the Center for Composite Materials and Associate Professor of Mechanical Engineering at the University of Delaware, Newark, DE 19716.

12a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

The development of residual stress is strongly influenced by processing history. Residual stress can have a significant effect on the mechanics and performance of composite structures by inducing warpage or initiating matrix cracks and delaminations. A fundamental study of the complex relationship between processing of thermosetting composites and residual stress has been conducted by the authors (Bogetti and Gillespie 1989, 1990a, 1990b). A cure simulation analysis coupled to a laminated plate theory model was used to study the development of processing-included stress and deformation in thick-section thermosetting composite laminates. Constitutive models were proposed to describe material behavior (chemical hardening and shrinkage) during cure. Thermal expansion and chemical cure shrinkage contribute to changes in material specific volume and represent important sources of internal loading included in the analysis. In this work we focus on the effects cure shrinkage has on residual stress and deformation development in thick-section glass/polyester and graphite/epoxy composite laminates. Additionally, model predictions of cure dependent modulus and dimensionless laminate curvature of graphite/epoxy (AS4/3501-6) cross-ply laminates are presented and found to be in good agreement with previously published experimental data.

14. SUBJECT TERMS
thermoset composites, thick laminates, cure simulation, residual stress, process-induced stress, laminated plate theory, processing history, chemical shrinkage, thermosetting resins, thermosetting plastics

15. NUMBER OF PAGES 31

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED

18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED

19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED

20. LIMITATION OF ABSTRACT UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18

INTENTIONALLY LEFT BLANK.

TABLE OF CONTENTS

INTENTIONALLY LEFT BLANK.

LIST OF FIGURES

INTENTIONALLY LEFT BLANK.

LIST OF TABLES

INTENTIONALLY LEFT BLANK.

ACKNOWLEDGMENT

This work was funded by the Army Research Office University Research Initiative Program and in cooperation with the U.S. Army Ballistic Research Laboratory at Aberdeen Proving Ground, Maryland. The authors are grateful for their support.

INTENTIONALLY LEFT BLANK.

1. INTRODUCTION

The development of residual stress in composite laminates is strongly influenced by processing history. Residual stress can have a significant effect on the mechanical performance of composite structures by inducing warpage or initiating matrix cracks and delaminations (Kau and Petrusha 1988; Kays 1985). Processing concerns associated with thermosetting composites become increasingly important for components of appreciable thickness. The most familiar problem is an increase in temperature resulting from the resin exothermic chemical reaction that may raise internal temperatures to levels inducing material degradation. A second concern is the complex gradients in temperature and degree of cure accentuated by increased thickness (Bogetti and Gillespie 1991).

Traditional residual stress analysis in thermosetting composite laminates is based on thermal expansion mismatch between adjacent plies, a uniform temperature drop from the cure temperature to ambient conditions, and no stress development prior to completion of the curing process (Griffin 1983; Hahn and Pagano 1975, 1976; Stango and Wang 1984). This approach may not be adequate for predicting the process-induced stresses in thick-section thermosetting composite laminates. The authors have shown that spatial solidification (resulting from complex temperature and degree-of-cure gradients) introduce several important mechanisms not accounted for in the traditional stress analysis methodology (Bogetti and Gillespie 1989, 1990a, 1990b).

The mechanisms governing stress development in thick-section composites are quite similar to those encountered in the manufacture of tempered glass (Lee, Rogers, and Woo 1965; Tackels and Crochet 1973; Crochet et al. 1974; Crochet and Denayer 1980). Such stresses result from the interactions between spatially varying thermal contractions, viscoelastic material response, and severe temperature gradients which develop during the quenching process. Early treatment of stress development due to viscoelastic material response in the presence of thermal gradients was based on the time-temperature superposition principle of rheologically simple material behavior (Muki and Sternberg 1961). This approach has been applied to study the macroscopic in-plane residual stress development during the quenching of a fully cured epoxy plate (Maneschy et al. 1986) and, more recently, to the quenching of thermoplastic matrix composites (Chapman et al. 1988).

As a thermosetting resin cures, the effective mechanical properties of the composite vary from a viscous liquid (negligible stiffness), in its uncured state, to a viscoelastic or elastic solid (high stiffness), in its fully cured state. During cure the resin undergoes significant increases in stiffness and volumetric shrinkage associated with the cross-linked polymerization reaction. The mechanical properties of the resin phase during cure are governed by competing mechanisms between chemical kinetic hardening and viscoelastic relaxation phenomena. Once fully cured, the resin exhibits traditional viscoelastic behavior at elevated temperatures and approaches elastic behavior at lower temperatures. Additionally, thermal expansion of the fully cured resin is the only mechanism contributing to changes in specific volume.

Complex temperature and degree-of-cure gradients which develop in thick-section thermosetting laminates induce spatially varying material response associated with resin stiffening and shrinkage as the chemical reaction progresses. Birefringence patterns have shown experimentally that temperature and degree-of-cure gradients have a significant effect on the development of residual stresses in thick thermosetting castings (Pusatcioglu et al. 1980). In a series of papers, Levitsky and Shaffer (1974, 1975) and Shaffer and Levitsky (1974) have studied the development of residual stresses, including temperature gradients and spatially varying "chemical hardening" effects on mechanical properties in isotropic thermosetting materials exhibiting no chemical shrinkage. Chemical shrinkage, however, represents a potentially significant change in specific volume (superimposed on changes in specific volume due to temperature) that exists in thermoset composites during the curing process.

Recently, Bogetti and Gillespie (1989, 1990a, 1990b) developed a model to predict process-induced stress in thick thermoset laminates employing a cure simulation analysis based on an incremental transient finite difference formulation that accounts for thermal and chemical interactions during processing. Material models were proposed to describe the resin modulus and volumetric (chemical) shrinkage as a function of degree of cure. A micromechanics model for continuous fiber composites was used to evaluate the instantaneous spatially varying mechanical properties, thermal expansion, and chemical shrinkage strains through the laminate thickness as a function of temperature and degree of cure. Process-induced stress and deformation predictions are based on an incremental laminate theory that includes temperature gradients, spatially varying cure-dependent mechanical properties, thermal expansion, and chemical shrinkage strains. Details of the cure simulation and process-induced stress models are presented elsewhere (Bogetti and Gillespie 1989, 1990a, 1990b, 1991).

The models developed demonstrate the complex interactions that exist between processing conditions (thermal history), cure kinetics, resin shrinkage, laminate thickness, and stress development in thick thermosetting composite laminates. Previous investigations have focused on the influence of thermal history and laminate thickness on stress development in thick glass/polyester laminates. In this work, the process-induced stress model is employed in parametric studies aimed at assessing the influence of resin chemical shrinkage and thermal expansion on stress development in thick-section glass/polyester and graphite/epoxy laminates. Model predictions are also compared with previously published experimental data for cure-dependent modulus and dimensionless laminate curvature of a graphite/epoxy (AS4/3501-6) cross-ply laminate (Hahn and Kim 1990).

2. ANALYSIS

2.1 Cure Simulation and Incremental Stress Analysis. The process-induced stress model employed in this investigation consists of three key submodels: (1) a cure simulation analysis, (2) material models to describe the resin behavior during cure, and (3) an incremental laminate plate theory stress analysis. The theoretical development and integration of these submodels is not presented here, as details are documented elsewhere (Bogetti and Gillespie 1989, 1990a, 1990b, 1991). Since this investigation focuses on the effects of resin behavior during cure (chemical hardening and shrinkage) on process-induced stress development, only these material models are reviewed in this report.

2.2 Material Models. The incremental stress analysis requires as input the mechanical properties and macroscopic strains of the composite, undergoing spatial chemical hardening and shrinkage in a transient thermal environment. The effective composite mechanical properties and strains are based on a unidirectional composite micromechanics model. The constituent fiber properties (constant), the resin properties and chemical shrinkage (cure dependent), and the fiber volume fraction are input. Two material models are proposed to describe the mechanical properties and volumetric shrinkage of the resin during cure. Changes in the resin properties directly influence the mechanical properties in the composite, and chemical shrinkage represents a significant source of internal loading during cure.

The first material model defines the instantaneous resin modulus, E_m, explicitly in terms of the degree of cure:

$$E_m = (1-\alpha)E_m^{\circ} + \alpha E_m^{\infty} + \gamma\alpha(1-\alpha)(E_m^{\infty} - E_m^{\circ}) \;, \tag{1}$$

where E_m° and E_m^∞ are the assumed fully uncured and fully cured resin moduli, respectively. The term γ, which must satisfy $(-1 < \gamma < 1)$, is introduced to quantify the competing mechanisms of stress relaxation and chemical hardening (Dillman and Seferis 1987). Increasing γ physically corresponds to a more rapid increase in modulus at lower degree of cure before asymptotically approaching the fully cured modulus. A value of $\gamma = 0$ was used to generate all the results presented in this work. The instantaneous resin shear modulus (also required input) is based on the isotropic material relation with ν_m assumed constant:

$$G_m = \frac{E_m}{2(1+\nu_m)} \quad . \tag{2}$$

The inherent limitation of this material model is that stress relaxation cannot be modeled explicitly (i.e., modulus is monotonically increasing with cure). Stress predictions resulting from this model, therefore, provide an upper bound estimate on process-induced stresses to be expected during cure. It is anticipated that this model would be most relevant to material systems undergoing rapid cure.

The second material model describes the volumetric chemical shrinkage of the resin during cure. No chemical shrinkage occurs after the cure is complete. The resin chemical shrinkage induces significant macroscopic strains in the composite, representing an important source of internal loading in thick-section laminates in addition to the traditionally recognized thermal expansion strains.

Neglecting higher order terms, the isotropic resin chemical shrinkage strain of a unit volume element of resin, $\Delta\varepsilon_r$, resulting from an incremental volume resin shrinkage, Δv_r, is given by

$$\Delta\varepsilon_r = \sqrt[3]{1+\Delta v_r} - 1 \quad . \tag{3}$$

The incremental volume resin shrinkage is based on an incremental change in degree of cure, $\Delta\alpha$, and the total volumetric shrinkage of the completely cured resin, V^T_{sh}, from the expression

$$\Delta v_r = \Delta\alpha V^T_{sh} \quad . \tag{4}$$

Incremental effective longitudinal and transverse chemical shrinkage strains in the composite, $\Delta\varepsilon^{ch}{}_L$ and $\Delta\varepsilon^{ch}{}_T$, respectively, are computed over each time increment in the cure-simulation. These strains are based on a micromechanics model (Hill 1965; Whitney and McCullough 1980) utilizing constant fiber properties, instantaneous cure-dependent properties of the resin, the resin chemical shrinkage strain increment, $\Delta\varepsilon_r$, a zero chemical shrinkage strain in the fiber, and the fiber volume fraction.

Incremental effective thermal expansion strains are also computed over each time increment during the simulation. These strains are based on temperature increments between time steps in the simulation, ΔT, and the instantaneous effective longitudinal and transverse thermal expansion coefficients of the composite, α_L and α_T, respectively. The incremental longitudinal and transverse strain increments in each ply are defined as:

$$\begin{aligned} \Delta\varepsilon^{th}{}_L &= \alpha_L \Delta T \\ \Delta\varepsilon^{th}{}_T &= \alpha_T \Delta T \quad . \end{aligned} \tag{5}$$

The expansion coefficients, α_L and α_T, are based on the micromechanics model utilizing constant fiber properties, cure dependent resin properties, constant thermal expansion coefficients of both the fiber and resin, as well as fiber volume fraction.

The total stress-free macroscopic processing-induced ply strains are computed from the superposition of the thermal and chemical strain increments during the curing process. Gradients in the material response to chemical shrinkage and thermal expansion strains during cure hardening represent significant sources of internal loading accounted for in the stress model employed in this investigation. Details of the material models presented here and the process-induced stress analysis methodology are presented elsewhere (Bogetti and Gillespie 1989, 1990a, 1990b, 1991).

3. RESULTS

Required input into the stress model is rather extensive; consequently, an input parameter summary is presented first. Model predictions for resin modulus development and volumetric shrinkage of the composite, associated with resin crosslinking during isothermal cure, are presented for glass/polyester and graphite/epoxy. Cure simulations are run at several temperatures for each system to examine the effects of cure kinetics with regard to the effects of significant through-the-thickness temperature gradients. The influence of chemical volumetric shrinkage on the residual stress profiles in both glass/polyester and graphite/epoxy laminates is examined. Finally, correlation of model predictions of transverse modulus development in unidirectional laminates and of curvature development in an unsymmetrical [0/90] graphite/epoxy laminate is made with previously published experimental results.

3.1 Input Parameter Summary. Input parameters used in this investigation are summarized in this section. The thermal properties of the composite systems are presented in Table 1. The complete description of the cure kinetics for the composite includes the total heat of reaction and a description of the rate of reaction as a function of temperature and degree of cure. Reaction rate expressions for the glass/polyester and graphite/epoxy material systems are different in form due to the inherent differences in the overall order of the reaction kinetics.

Table 1. Thermal Properties for Glass/Polyester and Graphite/Epoxy

Material	ρ[kg/m^3]	c_p[kJ/W°C]	k_z[kW/(m°C)]
Glass/Polyester	1.89×10^3	1.26	2.16×10^{-4}
Graphite/Epoxy	1.52×10^3	9.42×10^{-1}	4.46×10^{-4}

The glass/polyester material system consists of CYCOM 4102 polyester resin, manufactured by the American Cyanamid Corporation, and is reinforced with E-glass fibers (54% by volume). The reaction rate expression for the glass/polyester system is second-order overall in the sense that $(m_c + n_c = 2)$ (Adams 1988):

$$\frac{d\alpha}{dt} = A_c \exp(-\Delta E_c/RT)\alpha^{m_c}(1-\alpha)^{n_c}) \quad . \tag{6}$$

The constant R is the universal gas constant and T is absolute temperature. The exponents m_c and n_c, the preexponential coefficient, A_c, the activation energy, ΔE_c, and the total heat of reaction are listed in Table 2.

Table 2. Cure Kinetic Parameters for Glass/Polyester and Graphite/Epoxy

Glass/Polyester	
m_c	0.524
n_c	1.476
A_c[min.-1]	3.7×10^{22}
ΔE_c[J/mol]	1.67×10^{5}
H_r[kJ/kg]	77.5
Graphite/Epoxy	
A_1[min.-1]	2.102×10^{9}
A_2[min.-1]	-2.014×10^{9}
A_3[min.-1]	1.960×10^{5}
ΔE_1[J/mol]	8.07×10^{4}
ΔE_2[J/mol]	7.78×10^{4}
ΔE_3[J/mol]	5.66×10^{4}
H_r[kJ/kg]	198.9

The graphite/epoxy material system contains Hercules Corporation's 3501-6 resin, reinforced with unidirectional AS4 graphite fibers (67% by volume). The reaction rate expression for the graphite/epoxy system follows a markedly different form (Bogetti and Gillespie 1991):

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha)(1 - \alpha)(0.47 - \alpha) \quad for \quad (\alpha \leq 0.3)$$

and

$$\frac{d\alpha}{dt} = k_3(1 - \alpha) \qquad\qquad for \quad (\alpha > 0.3) \tag{7}$$

where k_1, k_2, and k_3 are defined by the Arrhenius rate expressions:

$$\begin{aligned} k_1 &= A_1 \exp(-\Delta E_1/RT) \\ k_2 &= A_2 \exp(-\Delta E_2/RT) \\ k_3 &= A_3 \exp(-\Delta E_3/RT) \quad . \end{aligned} \tag{8}$$

The preexponential coefficients A_1, A_2, and A_3, the activation energies, ΔE_1, ΔE_2, and ΔE_3, and the total heat of reaction for the graphite/epoxy composite are also summarized in Table 2.

The fiber and matrix constituent mechanical properties employed in all the parametric studies are summarized in Tables 3 and 4.

The results generated in this investigation are sensitive to both the time step size and the grid spacing used in the simulation. It is noted here that, for the range of processing variables and materials specific to this investigation, time step size and grid spacing increments were selected sufficiently small to yield converge solutions for all the example problems presented. Specifically, a time step size of 2.0 s and a grid spacing increment of 0.00127 m were used to generate all the results presented in this investigation.

3.2 Chemical Kinetic Effects on Material Models. Figure 1 shows the development of dimensionless resin modulus vs. time during isothermal cure for both the glass/polyester and graphite/epoxy systems. Isothermal cure isolates the behavior of the system induced by chemical kinetics from that induced by transient thermal effects. Temperatures at which the simulations were run correspond to a range of the respective manufacturer's suggested cure temperatures. Upon comparison of the curves, it is apparent that the cure of the polyester resin is much more violent than that of the epoxy. More importantly, we see that the polyester system, due to the extremely rapid nature of its cure behavior, is inherently much more sensitive to temperature variations than the epoxy system. Figure 2 illustrates the development of chemical volumetric shrinkage resulting from the cross-link polymerization reaction for both systems. Again, the rapid nature of the polyester cure with respect to the epoxy resin is noted (shrinkages have been nondimensionalized). We see that small temperature variations in the glass/polyester system may result in much more significant differences in degree of cure, and, thus, in instantaneous modulus and percent shrinkage, than in the graphite/epoxy system. Consequently, we anticipate a greater potential for stress development in the thick glass/polyester laminates due to its sensitivity to thermally induced gradients in degree of cure.

3.3 Volumetric Resin Shrinkage Effects on Stress Development.

3.3.1 Graphite/Epoxy. Figure 3 shows the predicted residual transverse stress profiles through the thickness of a 17.78-cm unidirectional graphite/epoxy laminate. Profiles are shown as a function of the magnitude of resin chemical shrinkage during cure. Note that the profile for the 0.0% cure shrinkage case

Table 3. Fiber and Matrix Constituent Properties

Property	Glass	Polyester	Graphite	Epoxy
E_1[MPa]	7.308×10^4	eqn. 1	2.068×10^5	eqn. 1
E_2[MPa]	7.308×10^4	eqn. 1	2.068×10^5	eqn. 1
v_{12}	0.22	0.40	0.20	0.35
v_{13}	0.22	0.40	0.20	0.35
v_{23}	0.22	0.40	0.50	0.35
G_{12}[MPa]	2.992×10^4	eqn. 2	2.758×10^4	eqn. 2
G_{13}[MPa]	2.992×10^4	eqn. 2	2.758×10^4	eqn. 2
G_{23}[MPa]	2.992×10^4	eqn. 2	2.758×10^4	eqn. 2
α_1	5.04×10^{-6}	7.20×10^{-5}	-9.00×10^{-7}	5.76×10^{-5}
α_2	5.04×10^{-6}	7.20×10^{-5}	7.20×10^{-6}	5.76×10^{-5}

Table 4. Resin Characteristics During Cure

Property	Polyester	Epoxy
E_m°	2.757	3.447
E_m^∞	2.757×10^3	3.447×10^3
V^T_{sh}	4.0 – 6.0	1.0 – 3.0

does not represent the minimum residual transverse stress, as there is a definite contribution from thermal expansion of the fiber and resin. The authors propose that the residual stress profile induced by thermal expansion effects alone is of the same magnitude but in direct competition with the stresses induced by chemical shrinkage during cure for the graphite/epoxy system being examined.

Figure 4 compares the residual transverse stress profiles induced by the isolated effects of thermal expansion and chemical shrinkage in a 17.78-cm laminate. Thus, profiles represent either the effects of thermal expansion only (CTE) or of volumetric shrinkage only (V^T_{sh} = 1.0, 3.0, and 6.0%). We see that the magnitude of the stresses developed by the thermal expansion strains is very close to that developed by the 1.5% volumetric shrinkage case. As the chemical cure shrinkage of the 3501-6 epoxy is thought

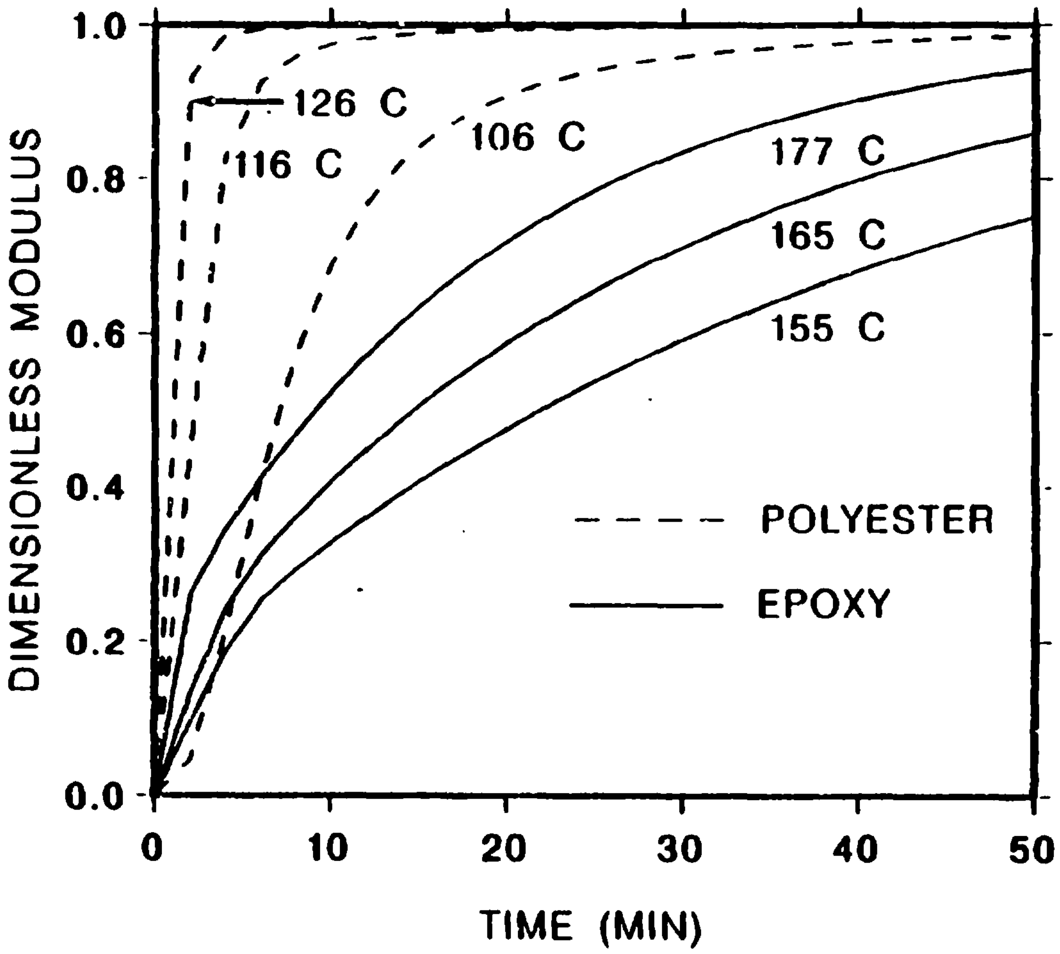

Figure 1. Normalized Resin Modulus Development During Isothermal Cure of Graphite/Epoxy and Glass/Polyester.

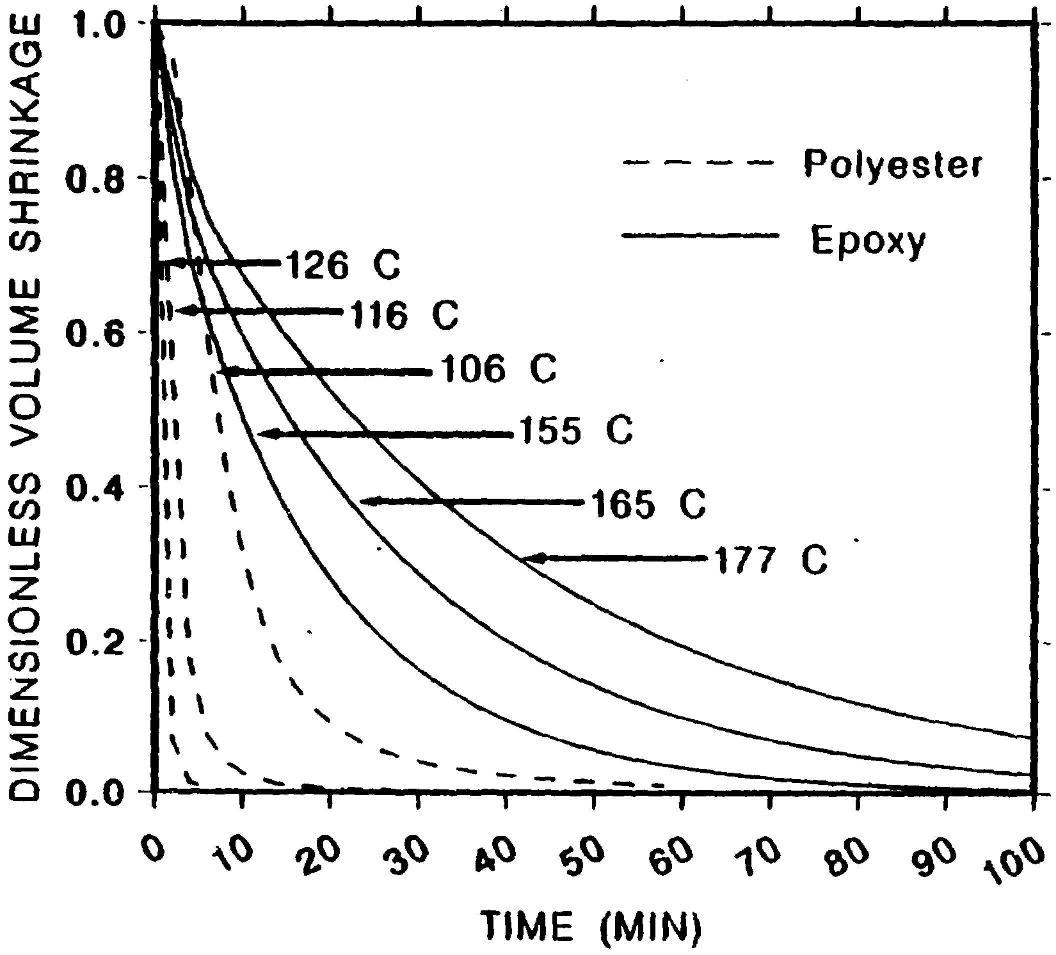

Figure 2. Normalized Resin Volumetric Shrinkage During Isothermal Cure of Graphite/Epoxy and Glass/Polyester.

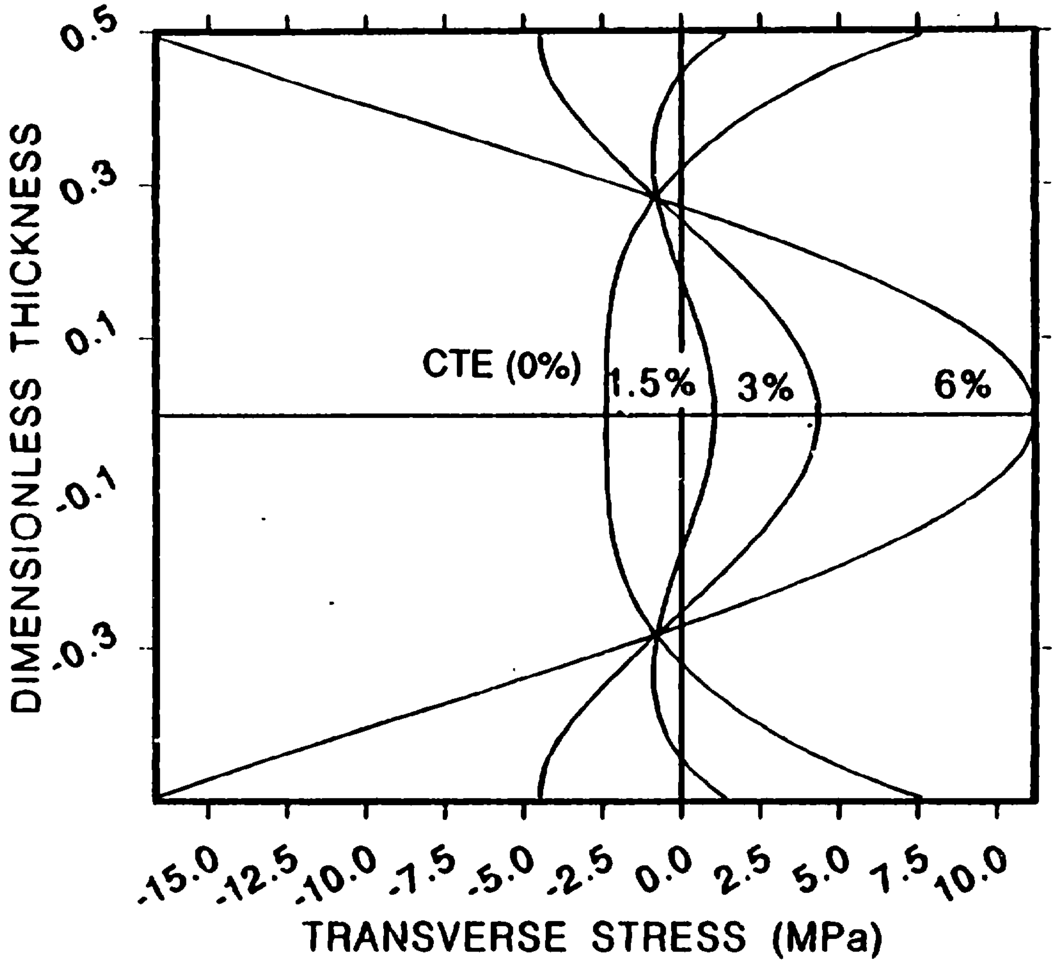

Figure 3. Predicted Transverse Residual Stress Profiles as a Function of the Magnitude of Resin Shrinkage in a 17.78-cm Graphite/Epoxy Laminate (Thermal Expansion and Resin Shrinkage Effects Superimposed).

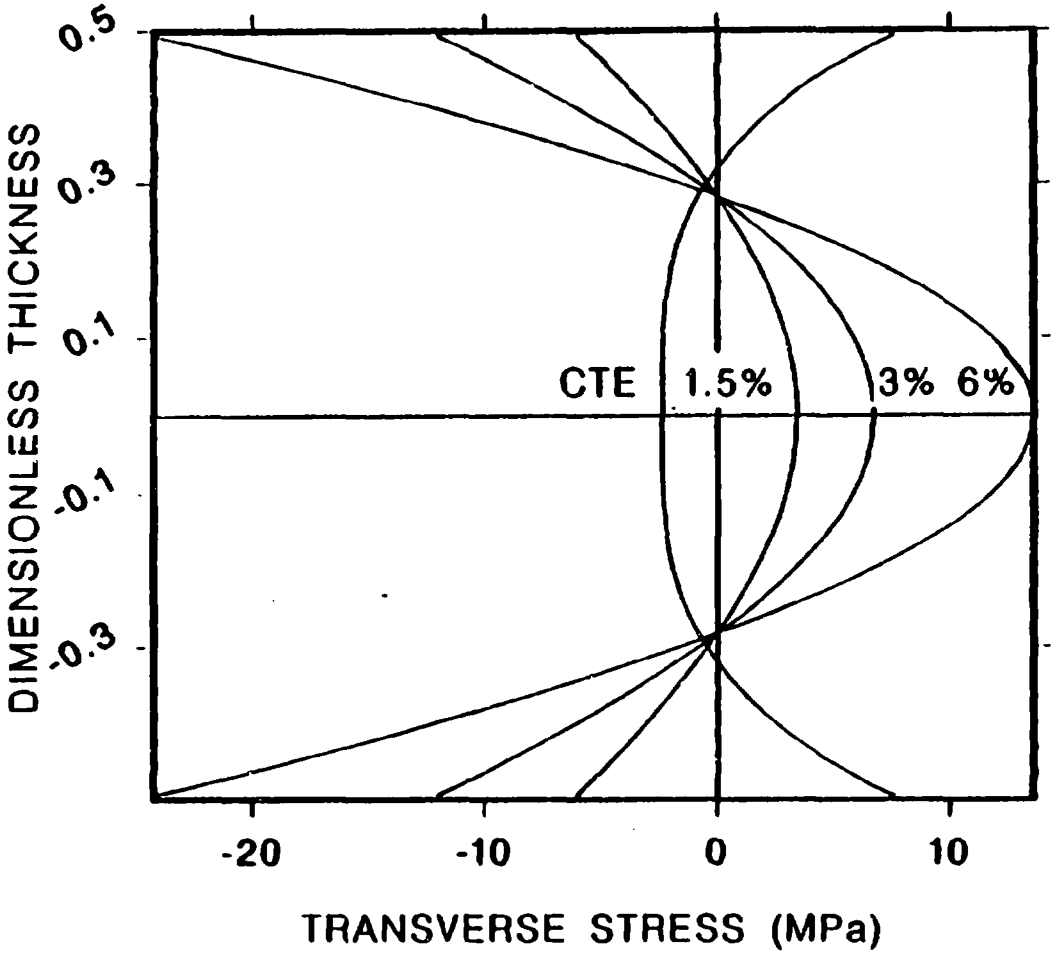

Figure 4. Thermal Expansion and Resin Shrinkage (Plotted Separately) Contributions to the Predicted Transverse Residual Stress Profiles in a 17.78-cm Graphite/Epoxy Laminate.

3.3.2 Glass/Polyester. A typical value for the cure shrinkage of the 4102 polyester resin is approximately 6.0%, as opposed to 1.5% for the 3501-6 epoxy. The increased contribution of the volumetric shrinkage, as well as the increased severity of the cure kinetics, leads us to expect significantly higher residual stress development in the glass/polyester system as compared to the graphite/epoxy system. Figure 5 illustrates process-induced transverse stress profiles for a 2.54-cm unidirectional glass/polyester laminate as a function of volumetric shrinkage. The reversal of the parabolic stress profiles is a result of the interactions of thickness and cure kinetics inducing a predominantly inside-to-outside cure rather than the outside-to-inside cure exhibited by the thicker graphite/epoxy sections. It is again demonstrated that the case with 0.0% resin shrinkage does not minimize process-induced stress development. Here it is demonstrated that a finite resin shrinkage, on the order of 1.0%, produces the nearly stress-free laminate. Note that the peak predicted residual stresses in this 2.54-cm glass/polyester laminate ($V^T_{sh} = 6\%$) are significantly larger than those predicted in the 17.78-cm graphite/epoxy laminate ($V^T_{sh} = 1.5\%$). This demonstrates the importance of volumetric resin shrinkage and cure kinetics on the process-induced residual stress development in thick-section laminates.

Figure 6 shows the predicted longitudinal residual stress profiles as a function of volumetric shrinkage for the same laminate. The magnitude of the residual stress in the fiber-dominated longitudinal direction is significantly lower than in the transverse direction, where processing strains are high. Also, it is worth noting that the volumetric shrinkage here—which most nearly produces a stress-free laminate in the longitudinal direction (approximately 2.0%)—is significantly larger than that for the transverse direction (approximately 1.0%). This indicates that it is inherently impossible to tailor the volumetric shrinkage of a resin to produce stress-free profiles in both the transverse and longitudinal directions. As such, it is more desirable to tailor the resin volumetric shrinkage to minimize the residual stress development in the weak transverse direction, where matrix cracking could more easily develop.

Figure 7 compares the transverse residual stress profiles induced by the isolated effects of thermal expansion strains (CTE) to the profiles resulting from volumetric shrinkage only ($V^T_{sh} = 1.0$, 3.0, and 6.0%) for the same 2.54-cm glass/polyester laminate. The thermal expansion effect is again seen to be opposite in sign to the shrinkage effects and of similar magnitude to the 1.0% shrinkage case. However, as the polyester resin actually undergoes approximately 6.0% shrinkage during cure, the effects of thermal expansion are nearly insignificant with respect to the total residual stress development in this example.

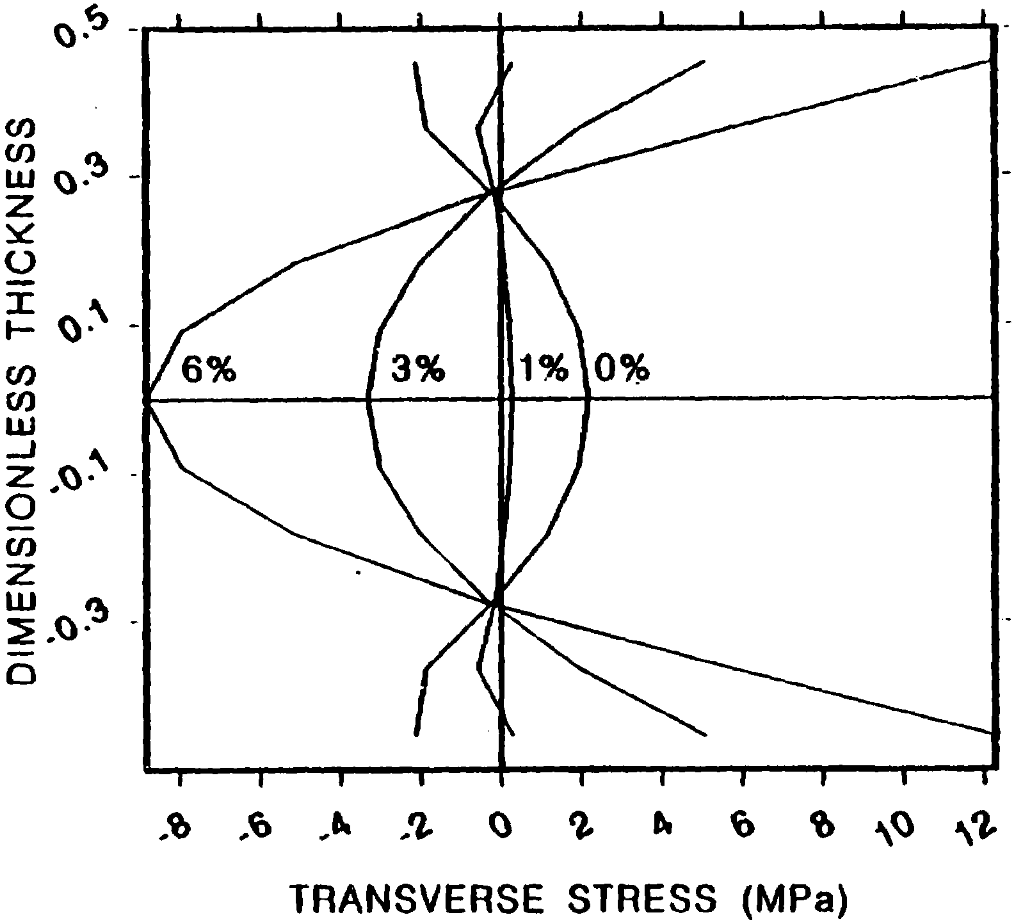

Figure 5. Predicted Transverse Residual Stress Profiles as a Function of Magnitude of Resin Shrinkage in a 2.54-cm Glass/Polyester Laminate (Thermal Expansion and Resin Shrinkage Effects Superimposed).

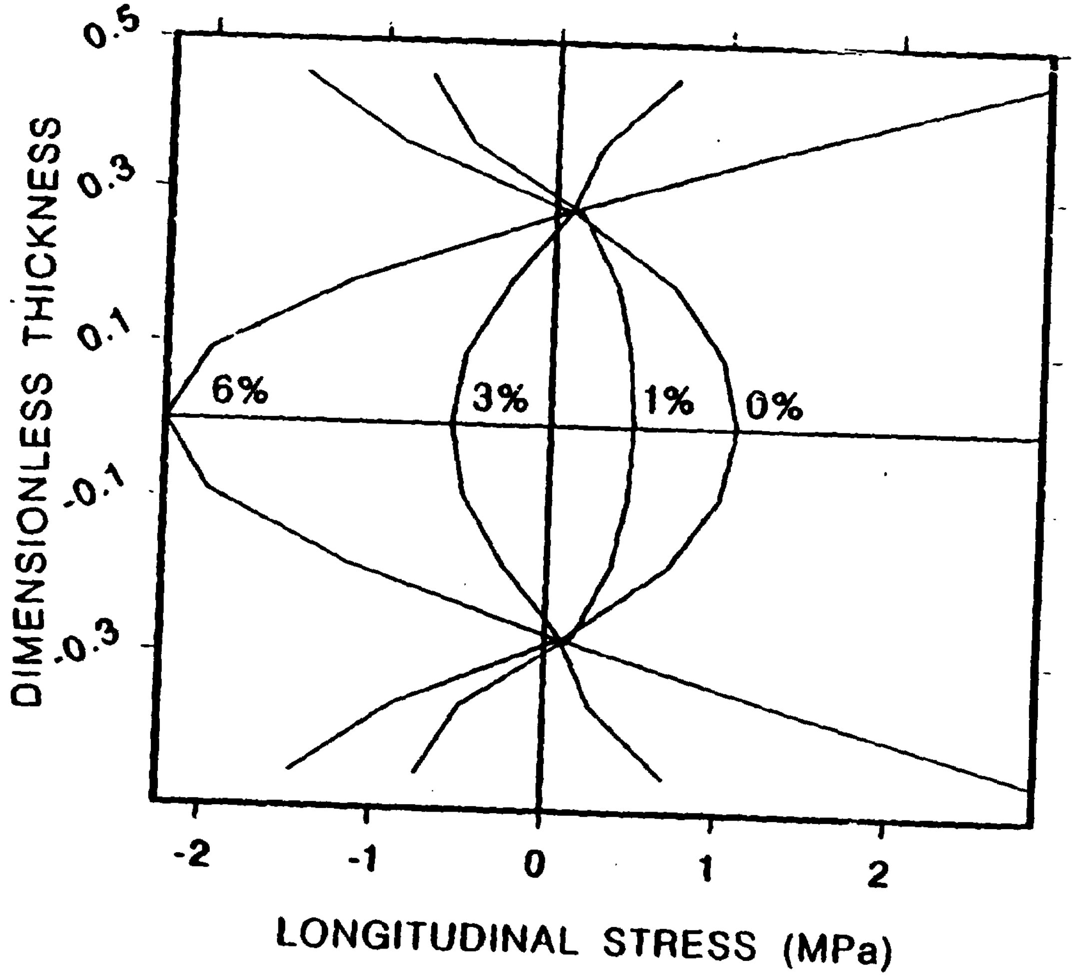

Figure 6. Predicted Longitudinal Residual Stress Profiles as a Function of Magnitude of Resin Shrinkage in a 2.54-cm Glass/Polyester Laminate (Thermal Expansion and Resin Shrinkage Effects Superimposed).

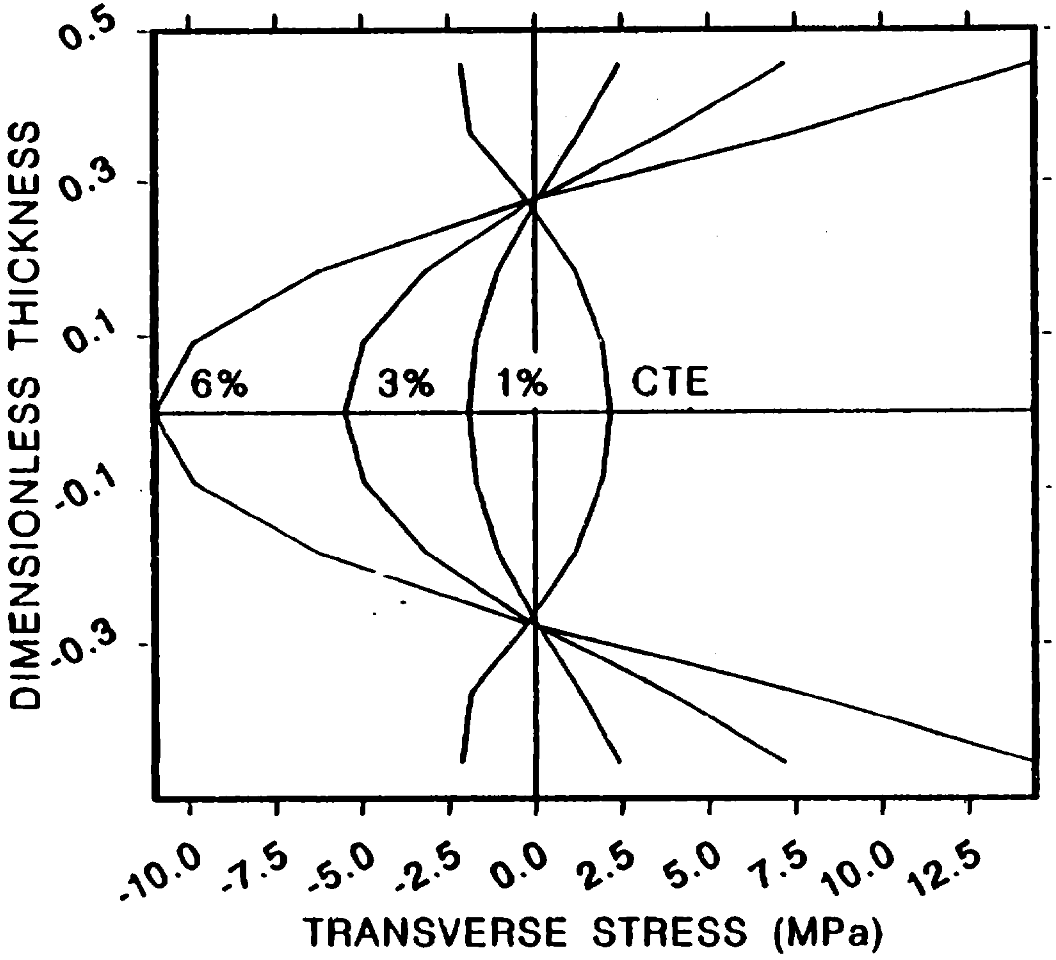

Figure 7. Thermal Expansion and Resin Shrinkage (Plotted Separately) Contributions on the Predicted Transverse Residual Stress Profiles in a 2.54-cm Glass/Polyester Laminate.

Predicted residual transverse stress profiles for a 5.08-cm glass/polyester laminate are illustrated as a function of the magnitude of volumetric shrinkage in Figure 8. Note the reversal of the parabolic stress profiles from the 2.54-cm laminate. This results from the fact that, in this case, the cure front propagates from the outside to the inside of the laminate due to the interactions between the thickness and the thermal history of the laminate. It is interesting to note that the magnitude of the residual transverse stresses in the 5.08-cm laminate is less than that of the 2.54-cm laminate. This is probably attributable to the competing effects of simultaneous cure front propagations (outside to inside and inside to outside), as is evidenced by the complex stress fields through the laminate thickness.

It is interesting to note that the magnitude of the chemical shrinkage required to counterbalance the residual transverse stresses induced by thermal expansion effects for a given system is not constant and is dependent upon the complex interactions between cure kinetics, laminate thickness, and processing history. From the inspection of Figure 5 it is apparent that for a 2.54-cm laminate (glass/polyester), a volumetric shrinkage of slightly over 1.0% will minimize transverse residual stress distributions. However, close examination of Figure 7 reveals that for a 5.08-cm laminate of the same system, a shrinkage of slightly less than 1.0% is necessary to minimize the transverse residual stresses.

3.4 Experimental Correlation. Hahn and Kim (1990) subjected several graphite/epoxy (T300/3501-6) unidirectional and unsymmetrical [0/90] laminates to interrupted cure cycles to monitor the development of transverse modulus (in the unidirectional laminates) and curvature induced by cure shrinkage and thermal strains (in the unsymmetrical laminates). The laminates were approximately 1 mm in thickness and the cure cycles followed the manufacturers recommended cure cycle (MRC). At each of a series of points during the MRC, a unidirectional and a cross-ply laminate were cooled to room temperature at 3° C/min. The unidirectional laminates were tensile tested to determine the transverse modulus, and the deflections of the unsymmetrical laminates were measured to determine process-induced curvatures. Figure 9 shows excellent agreement between the measured and predicted transverse modulus development based on the material model presented herein. Note that the horizontal axis refers to the time of cure stop. This indicates the time at which the MRC was interrupted and cooling to room temperature initiated and does not indicate the time of the full cycle to which the laminate was subjected, as not all laminates were cooled from the same temperature.

Figure 10 shows the development of nondimensionalized curvature (with respect to laminate thickness) as a function of the time of cure stop. Again, we see good agreement between measured and predicted values. Significant over-prediction of the curvature early in the cycle is thought to arise from the highly

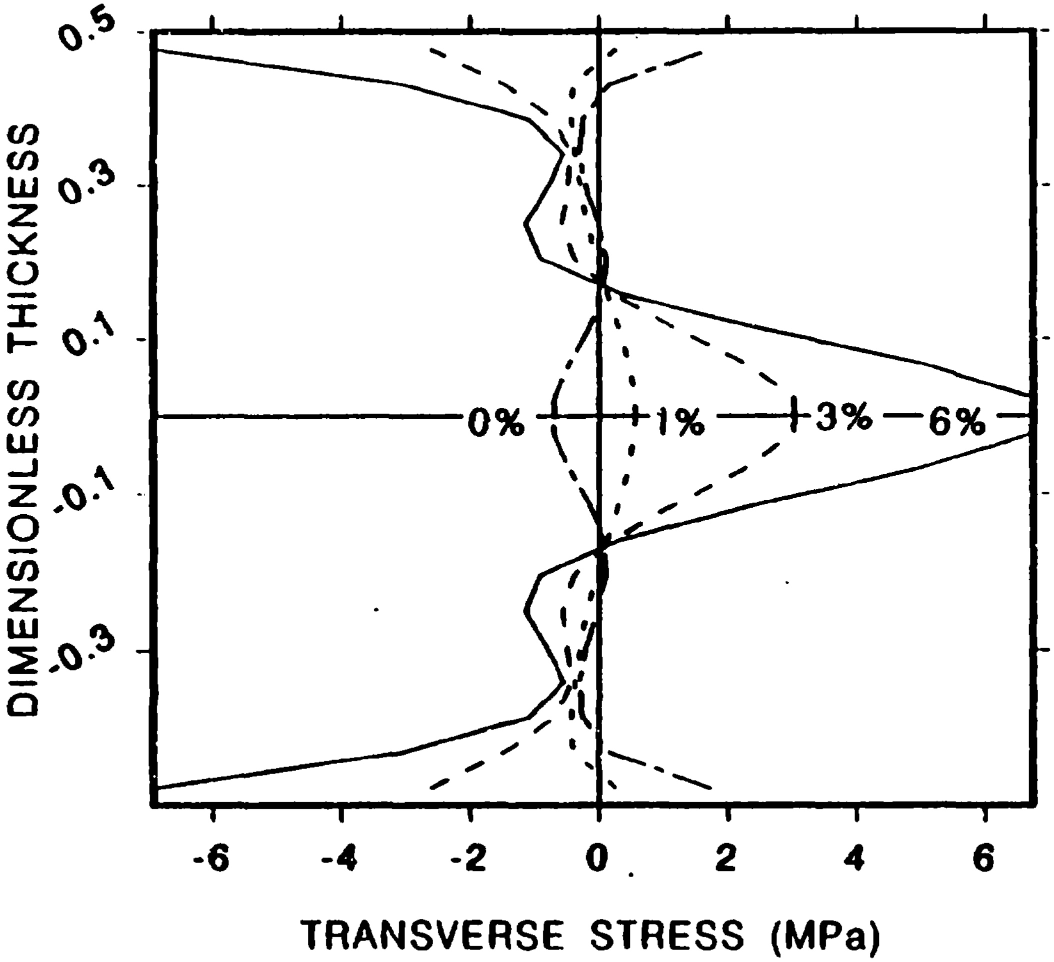

Figure 8. Predicted Transverse Residual Stress Profiles as a Function of Magnitude of Resin Shrinkage in a 5.08-cm Glass/Polyester Laminate (Thermal Expansion and Resin Shrinkage Effects Superimposed).

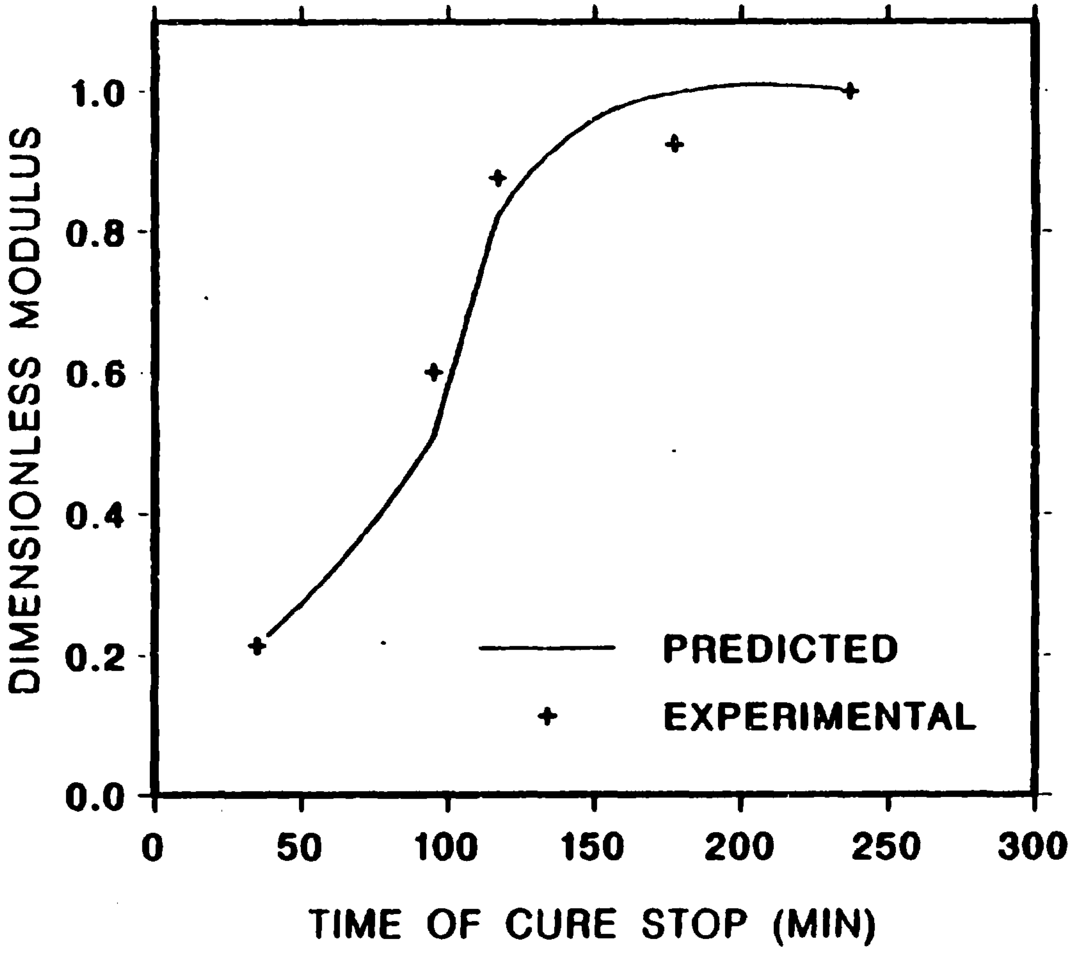

Figure 9. Experimental vs. Predicted Composite Transverse Modulus Development in an 8-ply Unidirectional Graphite/Epoxy Laminate.

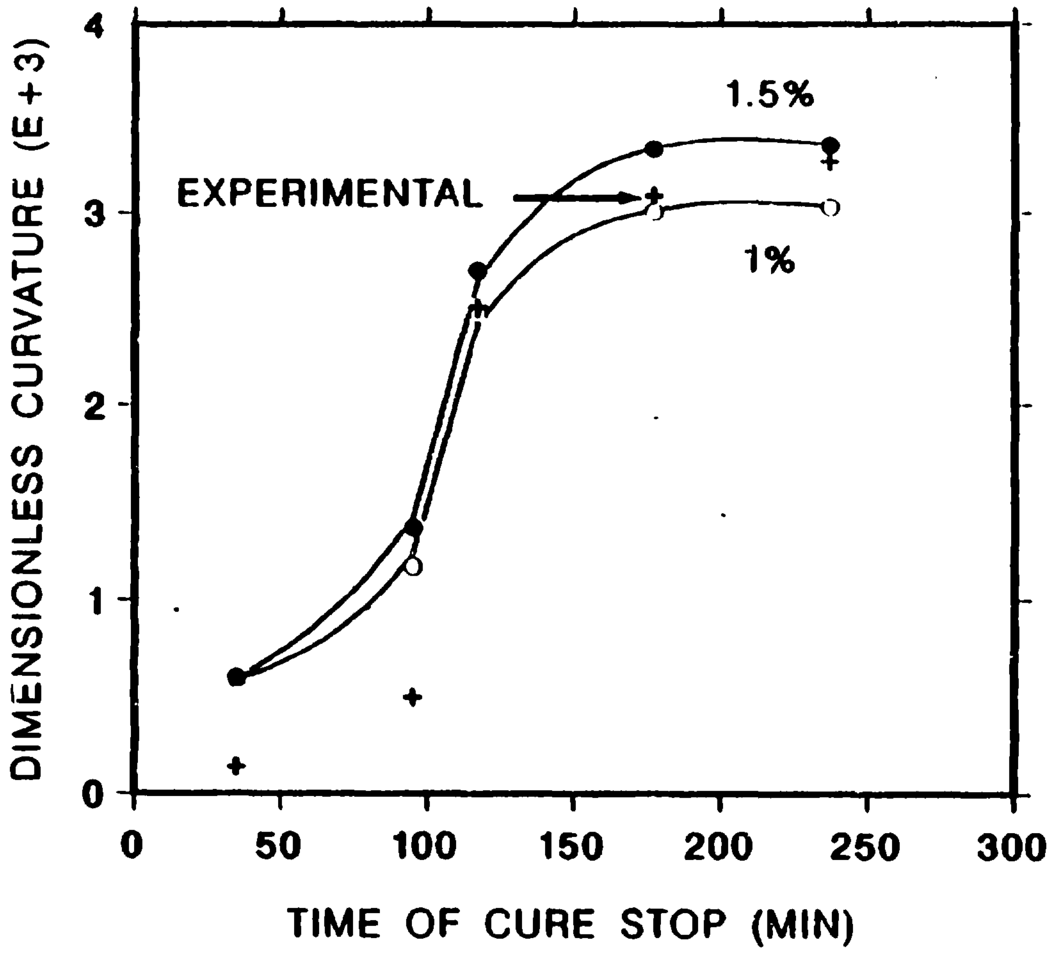

Figure 10. Experimental vs. Predicted Curvature During Cure of an 8-ply Unsymmetrical [0/90] Graphite/Epoxy Laminate.

viscoelastic behavior of the matrix which has not yet reached gelation. Also, the fracture surfaces of the tensile tested specimens in the region of the curvature over prediction exhibited little or no interfacial bonding between the fibers and the matrix, leading to a relatively unconstrained matrix and reduced stress development. By defining the gel point as the point at which the viscosity of the resin reaches 100 Pa-s, Hahn and Kim (1990) note that the curvature and the transverse modulus both increase sharply immediately after the gel point, possibly indicating that the development of residual stresses can be significantly affected by the mechanical properties of the resin before full cure has been reached.

4. CONCLUSIONS

A process-induced stress model, employing a cure simulation analysis and laminated plate theory, was used to study the evolution of macroscopic in-plane residual stresses during the cure of thick-section glass/polyester and graphite/epoxy laminates. Due to the neglect of thermal relaxation effects, model predictions are expected to provide upper bound estimates on residual stress development. Material models were proposed to describe chemical hardening and shrinkage of the resin as a function of degree of cure. The effects of cure kinetics and changes in specific volume of the resin during cure and cool down were found to be significant driving forces for the development of residual stresses. The model was employed to investigate the competing mechanisms of cure shrinkage and thermal expansion in residual stress development in thick-section laminates. It was demonstrated that the simultaneous minimization of residual stress in both the longitudinal and transverse directions through tailoring of the resin shrinkage is not possible. Furthermore, the optimum resin shrinkage to minimize residual stresses in the weak transverse direction is strongly dependent on reaction kinetics, specimen thickness, and the cure cycle employed during processing. Correlation of model predictions with previously published experimental data is in good agreement. This correlation provides confidence in the material models proposed to describe the resin behavior during cure and adds credibility to the methodology developed for predicting the evolution of residual stress and deformation in thick-section thermoset laminates during cure.

5. REFERENCES

Adams, D. C. "Cure Behavior of Unsaturated Polyester Resin Composites." Technical Report CCM-88-16, Center for Composite Materials, University of Delaware, Newark, DE, 1988.

Bogetti, T. A., and J. W. Gillespie, Jr. "Process-Induced Stress and Deformation in Thick-Section Thermosetting Composite Laminates." Paper presented at the 21st SAMPE Technical Conference, Atlantic City, NJ, September 1989.

Bogetti, T. A., and J. W. Gillespie, Jr. "Residual Stress and Deformation in Thick Laminate Composites Undergoing Chemical Hardening and Shrinkage." SPI Composite Institute's 45th Annual Conference Proceedings, Washington, DC, 12–15 February, 1990a.

Bogetti, T. A., and J. W. Gillespie, Jr. "Process-Induced Stress and Deformation in Thick-Section Thermoset Composite Laminates." BRL-TR-3182, U.S. Army Ballistic Research Laboratory, Aberdeen Proving Ground, MD, October 1990b.

Bogetti, T. A., and J. W. Gillespie, Jr. "Two-Dimensional Cure Simulation of Thick Thermosetting Composites." Journal of Composite Materials, vol. 25, no. 3, pp. 239–273, March 1991.

Chapman, T. J., J. W. Gillespie, Jr., R. B. Pipes, J-A. E. Manson, and J. C. Serefis. "Prediction of Processed-Induced Residual Stresses in Thermoplastic Composites." Technical Report CCM 88-36, Center for Composite Materials, University of Delaware, Newark, DE, 1988.

Crochet, M. J., and A. Denayer. "Transient and Residual Thermoviscoelastic Stresses in Glass." Journal of Applied Mechanics, vol. 47, pp. 254–260, 1980.

Crochet, M. J., J. De Bast, P. Gilard, and G. Tackels. "Experiential Study of Stress Relaxation During Annealing." Journal of Noncrystalline Solids, vol. 14, pp. 242–254, 1974.

Dillman, S. H., and J. C. Serefis. "Kinetic Viscoelasiticy for the Dynamic Mechanical Properties of Polymer Systems." Journal of Macromolecular Science-Chemistry, vol. 24, September 1987.

Griffin, O. H. "Three-Dimensional Curing Stresses in Symmetric Cross-ply Laminates with Temperature-Dependent Properties." Journal of Composite Materials, vol. 17, pp. 449–463, 1983.

Hahn, H. T., and K. S. Kim. "Residual Stress Development During Processing of Graphite/Epoxy Composites." Composite Science and Technology (submitted for publication) 1990.

Hahn, H. T., and N. J. Pagano. "Curing Stresses in Composite Laminates." Journal of Composite Materials, vol. 9, pp. 91–105, 1975.

Hahn, H. T., and N. J. Pagano. "Residual Stresses in Polymer Matrix Composite Laminates." Journal of Composite Materials, vol. 10, pp. 266–277, 1976.

Hill, R. "Theory of Mechanical Properties of Fibre-Strengthened Materials: III. Self-Consistent Model." Journal of Mechanics and Physics of Solids, vol. 13, pp. 189, 1965.

Kau, H., and L. A. Petrusha. "Dimensional Stability and Property Gradients in Thick SMC Sections." Technical Report GMR-6359, General Motors Research Laboratories, Warren, MI, 1988.

Kays, A. O. "Exploratory Development on Processing Science of Thick Section Composites." Technical Report AFWAL-TR-85-4090, Air Force Wright Aeronautical Laboratories, Wright Patterson AFB, OH, 1985.

Lee, E. H., T. G. Rogers, and T. C. Woo. "Residual Stresses in a Glass Plate Cooled Symmetrically From Both Surfaces." Journal of the American Ceramic Society, vol. 48, pp. 480–487, 1965.

Levitsky, M., and B. W. Shaffer. "Thermal Stresses in Chemically Hardening Elastic Media Application to the Molding Process." Journal of Applied Mechanics, vol. 41, pp. 647–651, September 1974.

Levitsky, M., and B. W. Shaffer. "Thermal Stresses in a Solid Sphere Cast From a Thermosetting Material." Journal of Applied Mechanics, vol. 42, pp. 651–655, September 1975.

Maneschy, C., Y. Miyano, M. Shimbo, and T. C. Woo. "Residual-Stress Analysis of an Epoxy Plate Subjected to Rapid Cooling on Both Surfaces." Experimental Mechanics, vol. 26, pp. 306–312, December 1986.

Muki, R., and E. Sternberg. "On Transient Thermal Stresses in Viscoelastic Materials With Temperature Dependent Properties." Journal of Applied Mechanics, vol. 28, pp. 193–207, June 1961.

Pusatcioglu, S. Y., J. C. Hassler, A. L. Frickle, and H. A. McGee, Jr. "Effect of Temperature Gradients on Cure and Stress Gradients in Thick Thermoset Castings." Journal of Applied Polymer Science, vol. 25, pp. 381–393, 1980.

Shaffer, B. W., and M. Levitsky. "Thermoelastic Constitutive Equations for Chemically Hardening Materials." Journal of Applied Mechanics, vol. 41, pp. 652–657, September 1974.

Stango, R. J., and S. S. Wang. "Process-Induced Residual Thermal Stresses in Advanced Fiber-Reinforced Composite Laminates." Journal of Engineering for Industry, vol. 106, pp. 48–54, 1984.

Tackels, G., and M. J. Crochet. "Thermal Stresses During Annealing of a Glass Ribbon." Rheologica Acta, vol. 12, pp, 330–336, 1973.

Whitney, J. M., and R. L. McCullough. "Analytical Design Methods." Composites Design Guide, Center for Composite Materials, University of Delaware, Newark, DE, 1980.

No. of Copies	Organization
2	Administrator Defense Technical Info Center ATTN: DTIC-DDA Cameron Station Alexandria, VA 22304-6145
1	Commander U.S. Army Materiel Command ATTN: AMCAM 5001 Eisenhower Ave. Alexandria, VA 22333-0001
1	Commander U.S. Army Laboratory Command ATTN: AMSLC-DL 2800 Powder Mill Rd. Adelphi, MD 20783-1145
2	Commander U.S. Army Armament Research, Development, and Engineering Center ATTN: SMCAR-IMI-I Picatinny Arsenal, NJ 07806-5000
2	Commander U.S. Army Armament Research, Development, and Engineering Center ATTN: SMCAR-TDC Picatinny Arsenal, NJ 07806-5000
1	Director Benet Weapons Laboratory U.S. Army Armament Research, Development, and Engineering Center ATTN: SMCAR-CCB-TL Watervliet, NY 12189-4050
(Unclass. only) 1	Commander U.S. Army Rock Island Arsenal ATTN: SMCRI-TL/Technical Library Rock Island, IL 61299-5000
1	Director U.S. Army Aviation Research and Technology Activity ATTN: SAVRT-R (Library) M/S 219-3 Ames Research Center Moffett Field, CA 94035-1000
1	Commander U.S. Army Missile Command ATTN: AMSMI-RD-CS-R (DOC) Redstone Arsenal, AL 35898-5010
1	Commander U.S. Army Tank-Automotive Command ATTN: ASQNC-TAC-DIT (Technical Information Center) Warren, MI 48397-5000
1	Director U.S. Army TRADOC Analysis Command ATTN: ATRC-WSR White Sands Missile Range, NM 88002-5502
1	Commandant U.S. Army Field Artillery School ATTN: ATSF-CSI Ft. Sill, OK 73503-5000
(Class. only) 1	Commandant U.S. Army Infantry School ATTN: ATSH-CD (Security Mgr.) Fort Benning, GA 31905-5660
(Unclass. only) 1	Commandant U.S. Army Infantry School ATTN: ATSH-CD-CSO-OR Fort Benning, GA 31905-5660
1	WL/MNOI Eglin AFB, FL 32542-5000
	Aberdeen Proving Ground
2	Dir, USAMSAA ATTN: AMXSY-D AMXSY-MP, H. Cohen
1	Cdr, USATECOM ATTN: AMSTE-TC
3	Cdr, CRDEC, AMCCOM ATTN: SMCCR-RSP-A SMCCR-MU SMCCR-MSI
1	Dir, VLAMO ATTN: AMSLC-VL-D
10	Dir, USABRL ATTN: SLCBR-DD-T

No. of
Copies Organization

11 Director
Benet Weapons Center
U.S. Army Armament Research, Development,
and Engineering Center
ATTN: SMCAR-CCB,
J. Keane
T. Allen
J. Vasilakis
G. Friar
J. Zweig
L. Johnson
T. Simkins
V. Montvori
J. Wrzochalski
G. D'Andrea
R. Hasenbein
Watervliet, NY 12189-4050

7 Commander
U.S. Army Armament Research, Development,
and Engineering Center
ATTN: SMCAR-CCH-T,
S. Musalli
P. Christian
K. Fehsal
SMCAR-CCH-V, E. Fennell
SMCAR-CCH, J. DeLorenzo
SMCAR-CC,
R. Price
J. Hedderich
Picatinny Arsenal, NJ 07806-5000

2 Commander
U.S. Army Armament Research, Development,
and Engineering Center
ATTN: SMCAR-TD,
V. Linder
T. Davidson
Picatinny Arsenal, NJ 07806-5000

1 Commander
U.S. Army Armament Research, Development,
and Engineering Center
Production Base Modernization Activity
ATTN: AMSMC-PBM-K
Picatinny Arsenal, NJ 07806-5000

No. of
Copies Organization

1 Commander
U.S. Army Belvoir RD&E Center
ATTN: STRBE-JBC, C. Kominos
Fort Belvoir, VA 22060-5606

2 Commander
U.S. Army Laboratory Command
Harry Diamond Laboratories
ATTN: SLCHD-TS-NT, A. Frydman
2800 Powder Mill Rd.
Adelphi, MD 20783-1197

1 Commander
U.S. Army Laboratory Command
ATTN: AMSLC-TD, R. Vitali
Adelphi, MD 20783-1145

1 Commander
U.S. Army Missile Command
ATTN: AMSMI-RD, W. McCorkle
Redstone Arsenal, AL 35898

3 Commander
U.S. Army Armament Research, Development,
and Engineering Center
ATTN: SMCAR-FSA-M,
R. Botticelli
F. Diorio
SMCAR-FSA,
C. Spinelli
Picatinny Arsenal, NJ 07806-5000

1 Project Manager
Advanced Field Artillery System
Picatinny Arsenal, NJ 07806-5000

1 Commander
Watervliet Arsenal
ATTN: SMCWV-QA-QS, K. Insco
Watervliet, NY 12189-4050

2 Project Manager
SADARM
Picatinny Arsenal, NJ 07806-5000

No. of Copies	Organization
6	Project Manager Tank Main Armament Systems ATTN: SFAE-AR-TMA, COL Hartline SFAE-AR-TMA-MD, C. Kimker W. Lang SFAE-AR-TMA-ME, K. Russell H. Yuen D. Guzowitz Picatinny Arsenal, NJ 07806-5000
2	PEO-Armaments ATTN: SFAE-AR-PM, D. Adams T. McWilliams Picatinny Arsenal, NJ 07806-5000
2	Commander Wright-Patterson Air Force Base ATTN: AFWAML, J. Whitney R. Kim Dayton, OH 45433
1	Commander DARPA ATTN: J. Kelly 1400 Wilson Blvd. Arlington, VA 22209
2	Director U.S. Army Materials Technology Laboratory ATTN: SLCMT-MEC, B. Halpin T. Chou Watertown, MA 02172-0001
1	Naval Research Laboratory Code 6383 ATTN: I. Wolock Washington, DC 20375-5000
2	David Taylor Research Center ATTN: R. Rockwell W. Phyillaier Bethesda, MD 20054-5000
1	David Taylor Research Center Ship Structures and Protection Department Code 1702 ATTN: J. Corrado Bethesda, MD 20084
5	Director Lawrence Livermore National Laboratory ATTN: R. Christensen S. deTeresa W. Feng J. Lepper F. Magness P.O. Box 808 Livermore, CA 94550
2	Pacific Northwest Laboratory A Division of Battelle Memorial Institute Technical Information Section ATTN: M. Smith M. Garnich P.O. Box 999 Richland, WA 99352
6	Director Sandia National Laboratories Applied Mechanics Department, Division-8241 ATTN: C. Robinson G. Benedetti W. Kawahara K. Perano D. Dawson P. Nielan P.O. Box 969 Livermore, VA 94550-0096
1	Los Alamos National Laboratory ATTN: D. Rabern MEE-13, Mail Stop J-576 P.O. Box 1633 Los Alamos, NM 87545
3	University of Delaware Center for Composite Materials ATTN: J. Gillespie B. Pipes M. Santare 201 Spencer Laboratory Newark, DE 19716

No. of
Copies Organization

2 North Carolina State University
Civil Engineering Department
ATTN: W. Rasdorf
L. Spainhour
P.O. Box 7908
Raleigh, NC 27696-7908

1 University of Utah
Department of Mechanical and Industrial Engineering
ATTN: S. Swanson
Salt Lake City, UT 84112

1 Stanford University
Department of Aeronautics and Aeroballistics
Durant Building
ATTN: S. Tsai
Stanford, CA 94305

1 Pennsylvania State University
Department of Engineering Science and Mechanics
ATTN: T. Hahn
227 Hammond Bldg.
University Park, PA 16802

1 University of Illinois at Urbana-Champaign
National Center for Composite Materials Research
216 Talbot Laboratory
ATTN: J. Economy
104 South Wright St.
Urbana, IL 61801

2 Olin Corporation
Flinchbaugh Division
ATTN: E. Steiner
B. Stewart
P.O. Box 127
Red Lion, PA 17356

1 Olin Corporation
ATTN: L. Whitmore
10101 9th St., North
St. Petersburg, FL 33702

No. of
Copies Organization

3 Alliant Techsystems, Inc.
ATTN: C. Candland
J. Bode
K. Ward
5640 Smetana Dr.
Minnetonka, MN 55343

1 Chamberlain Manufacturing Corporation
Research and Development Division
ATTN: T. Lynch
550 Esther St.
P.O. Box 2335
Waterloo, IA 50704

1 Custom Analytical Engineering Systems, Inc.
ATTN: A. Alexander
Star Route, Box 4A
Flintstone, MD 21530

2 Institute for Advanced Technology
ATTN: T. Kiehne
H. Fair
4030-2 W. Braker Ln.
Austin, TX 78759

USER EVALUATION SHEET/CHANGE OF ADDRESS

This Laboratory undertakes a continuing effort to improve the quality of the reports it publishes. Your comments/answers to the items/questions below will aid us in our efforts.

1. BRL Report Number BRL-TR-3380 Date of Report July 1992

2. Date Report Received ______

3. Does this report satisfy a need? (Comment on purpose, related project, or other area of interest for which the report will be used.) ______

4. Specifically, how is the report being used? (Information source, design data, procedure, source of ideas, etc.) ______

5. Has the information in this report led to any quantitative savings as far as man-hours or dollars saved, operating costs avoided, or efficiencies achieved, etc? If so, please elaborate. ______

6. General Comments. What do you think should be changed to improve future reports? (Indicate changes to organization, technical content, format, etc.) ______

CURRENT ADDRESS

Name ______
Organization ______
Address ______
City, State, Zip Code ______

7. If indicating a Change of Address or Address Correction, please provide the New or Correct Address in Block 6 above and the Old or Incorrect address below.

OLD ADDRESS

Name ______
Organization ______
Address ______
City, State, Zip Code ______

(Remove this sheet, fold as indicated, staple or tape closed, and mail.)