Simulation of Cure Volume Shrinkage Stresses on Carbon/Vinyl Ester Composites in Microindentation Testing

Tom Mase, Lanhong Xu, Lawrence T. Drzal
Composite Materials and Structures Center
Michigan State University

Abstract

Composites made with carbon fibers and vinyl ester have significant higher processing volume shrinkage compared to composites made with epoxies. During the curing, vinyl esters experience as much as three times the volume shrinkage as compared to epoxies (10 %Vol versus 3-4 %Vol). This difference in cure volume shrinkage may be the reason that the mechanical properties of carbon/vinyl esters are low compared to that of carbon/epoxy. Cure volume shrinkage of neat resins have been measured using a dilatometer. Interfacial shear strength (IFSS) measurements for different cure volume shrinkage were completed showing a reduction in strength as the cure volume shrinkage increased. LS-DYNA was used to model the volume cure shrinkage and resulting interface/interphase properties. Modeling results are dependent on the specific representative volume element (RVE) and boundary conditions used in the simulation. Cure volume shrinkage was modeled using a temperature drop on thermoelastic material (*MAT_ORTHOTROPIC_THERMAL). Following the temperature drop, the fiber was loaded with a rigid, spherical indenter to simulate the IFSS test (at constant temperature). Simulated resultant fiber-interphase, interphase-matrix, and fiber-matrix (in the case of no sizing) are reported as a function of cure volume shrinkage. Shearing stress distributions at the fiber-interphase and interphase-matrix are also presented.

Introduction

Thermoset vinyl ester resins have good toughness and chemical resistance compared to unsaturated polyester, but their combination with carbon fibers often results in low mechanical properties due to the low fiber-matrix adhesion[1-3]. A possible reason for the reduced mechanical properties may be the cure volume shrinkage (CVS) of vinyl ester[4]. As the vinyl ester shrinks during curing residual stresses remain in the composite material. Shrinkage residual stresses could be a very important factor lowering the matrix-fiber adhesion. Epoxies have better adhesion which may be attributed to their 3-4% cure volume shrinkage versus 5-10% shrinkage for vinyl esters [4-6]. It has been shown that application of lightly cross-linked Diglycidyl Ether of Biphenol A (DGEBA) cured with Aliphatic Polyether Triamine (Jeffamine T-403) epoxy sizing to the carbon fiber surface creates a beneficial interphase between the vinyl ester and carbon fiber [2,3,7,8].

Recent work examined the influence of matrix shrinkage of several resins by comparing IFSS data [9]. Neat resin cure shrinkage for Derakane 411-C50 (Dow Chemical) and Fuchem 891 (Shanghai Fuchem Chemical Co.) was measured using a custom made dilatometer. Both of these expoxies used styrene as a dilutent (50% for D411-C50 and 35% for Fuchem 981). Use of these resins along with three different initiators, CHP-5, CoNap, and MEKP, produced resins having 1.73, 5.85, 7.18, and 8.21 percent cure volume shrinkage. Composites made with these resins and carbon graphite (Hexcel, Inc.) showed an increase in modulus and decrease in IFSS as the cure volume shrinkage increased [13].

Another aspect of Ref. 9 was finite element modeling of the cure volume shrinkage followed by loading the end of the fiber as in an IFSS experiment. It was shown that the von Mises stress

(a measure of distortional strain energy) increased as cure volume shrink increased in the resin. The volume shrinkage was modeled by a constant temperature drop to a fixed value which was then held. To determine the appropriate temperature drop associated with experimental results, the matrix expansion coefficients was set to known value 80×10^{-6} and the temperature change required to get measured volume shrinkage was calculated. Interphase cure volume shrinkage of 1.58% was assumed to calculate the interphase thermal expansion coefficient required. After that, the loading tup was given a prescribed displacement into the fiber. The magnitude of the tup prescribed displacement was selected to yield a load of approximately 6-*g*.

Measurement of Cure Volume Shrinkage

Different brands or recipes of vinyl esters can exhibit substantially different cure shrinkage. To measure the cure shrinkage a custom dilatometer was constructed in the lab consisting of vinyl ester in a test tube covered with silicon oil. The top of the tube was sealed with a partially filled pipette protruding. As the vinyl ester cured the level of the oil in the pipette was measured to obtain a cure shrinkage. Figure 1 gives shrinkage values for the two vinyl ester systems used where methyl ethyl ketone peroxide (MEKP) and cumene hydroperoxide (CHP) were initiators, cobalt naphanate (CoNap) was the promoter, and dimethyl aniline (DMA) was the accelerator.
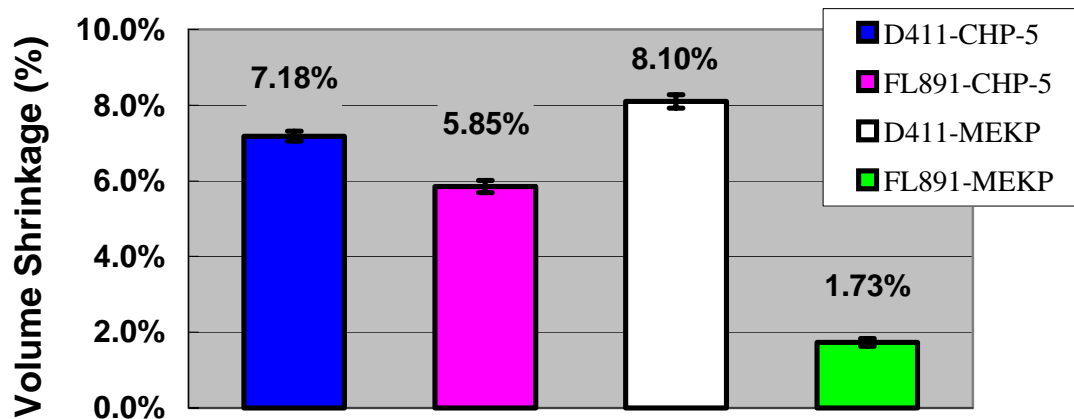

Figure 1 Cure volume shrinkage of different vinyl esters.

Table 1 Vinyl ester constituents

Cure Shrink, %	Vinyl Ester	CHP-5	MEKP	CoNap	DMA
8.10	D411-C50	---	2.85%	0.14%	---
7.18	D411-C50	2.00%	---	0.30%	0.10%
5.85	Fuchem 981	1.40%	---	0.21%	0.07%
1.73	Fuchem 981	---	2.00%	0.10%	---

Modeling Nanoindentation

A representative unit cell must be chosen for the simulation of the microindenation method for interfacial mechanical properties. Two common fiber array models are square- and hexagonal-packed arrays [11]. Associated with each packing array is a repeating unit cell that is taken to represent the composite. In this paper, the square-packed array was used as is shown in Fig. 2. There are symmetries associated with this fiber packing scheme that greatly reduce the computation time for simulation. The *x*- and *y*-axes shown in Fig. 3 are axes of symmetry allowing for the simulation of only one quarter of the fiber cross section.

The remaining two sides of the quarter unit cell may be modeled as either symmetric or free. If the composite edges were unconstrained as the resins undergo cure shrinkage it would be appropriate to model the remaining sides as free. Overall the composite would contract upon an individual fiber. On the other hand, the microindentation composite specimen is normally potted in a bedding material. This bedding material could constrain the composite sides implying the remaining sides may be best modeled as fixed boundaries as in Ref. 10.
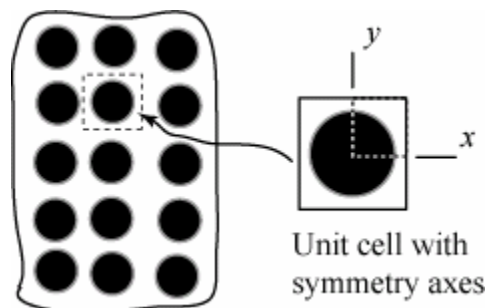

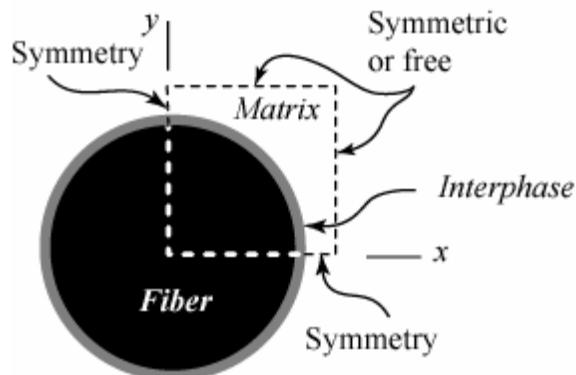Figure 2 Square packed array with unit cell.

Figure 3 Detail of simulation unit cell.

In this paper, the effect of the different boundary conditions on the resulting stresses along the fiber interface was examined. Additionally, the fiber volume fraction and the amount of resin cure shrinkage were examined by presenting the resulting stresses and forces between the matrix and the interphase. Two distinct phases were simulated: a temperature drop to model the curve volume shrinkage followed by loading the fiber end by a spherical indenter holding the temperature constant.

A summary of the fiber and matrix properties used in this study are given in Table 2. A fiber diameter of 7 *µm* was used along with an interphase thickness of 0.16 *µm* for all cases. Two fiber volume ratios were examined: 60 and 27%. Since the interphase is small in dimension it is

worth noting how the measurements of Table 2 were made. It was assumed that the interphase is isotropic and bulk material properties can be measured using a MTS nanoindentation machine as described in Ref. 12. Coefficient of thermal expansion for the interphase was made variable to achieve the volume shrinkage measured in the laboratory. In the fiber direction the coefficient of thermal expansion was set to zero to avoid a protruding fiber for subsequent loading. The actual specimen is prepared for nanoindentation by polishing the surface smooth which is why this was done in the simulation.

Table 2 Thermomechanical properties used for simulation

Property	Fiber	Interphase	Matrix
E_1, E_2 (GPa)	21	2.11	3.38
E_3 (GPa)	241	2.11	3.38
v_{12}, v_{13}	0.2	0.356	0.356
v_{23}	0.25	0.356	0.356
G_{12} (GPa)	8.3	0.778	1.246
G_{13}, G_{23} (GPa)	21	0.778	1.246
α_1, α_2 (10^{-6} °C^{-1})	8.5	Variable	80
α_3 (10^{-6} °C^{-1})	0	0	0
ρ (g/cm^3)	1.78	1.16	1.12

Modeling Results

The finite element simulation was conducted using LS-DYNA, a commercial code having options for either implicit or explicit formulation. Only explicit modeling was used for simulations presented in this paper. In such formulation, the simulation is unconditionally stable provided that the time step remains smaller than a critical value called the Courant criterion. Explicit simulation involves many computationally efficient time steps. The Courant criterion time step is equivalent to the time it takes a wave to propagate across the smallest element dimension. Thus, it depends on the square root of the material stiffness divided by the density. Some problems, like microindentation, do not have much kinetic energy associated with them and to make the computations more time efficient the mass is scaled up to increase the time step. This was done in the current work. All densities (fiber, interphase, and matrix) were scaled up 10^4 from the values of Table 2. Additionally, the cure shrinkage was completed in 0.025 s and the fiber loading was done in the following 0.025 s. These times were chosen to avoid significant stress waves from developing in the cure shrinkage phase of simulation and to reduce computation time to reasonable values. To check that kinetic energy is not playing a significant role in the results, Fig. 4 shows the kinetic, internal, and total energy for one of the simulations. As the tup loads the fiber the kinetic energy is negligible compared to the internal energy. Simulation runs took approximately 4 hours to run. The model consisted of 23,655 nodes and 20,176 elements (Fig. 5). The length of the fiber modeled was 20 times the fiber diameter. This value has been shown to be sufficient to allow the stresses to decay to nominal values [10].

Conclusions

Explicit 3-D finite element analysis has been used to model microindentation testing having cure volume shrinkage (CVS) as a parameter. Using experimental data from previous work as a guideline, the following may be stated with regards to the modeling:

- Increasing the cure volume shrinkage from 1.73 to 7.32 percent increases the maximum von Mises stress (a measure of distortional energy), decreases the peel stress, and marginally increases the shear stress in the matrix at the interphase boundary.
- Modeling the remaining boundaries as free (boundaries that are all matrix) decreased the von Mises and peel stresses while increasing the shear stress in the matrix adjacent to the interphase.
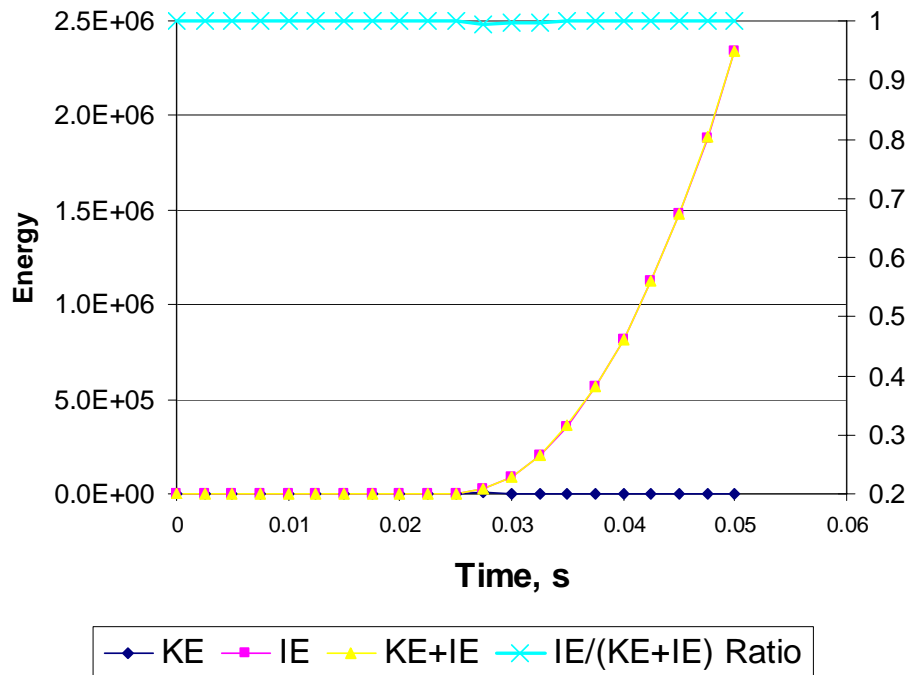

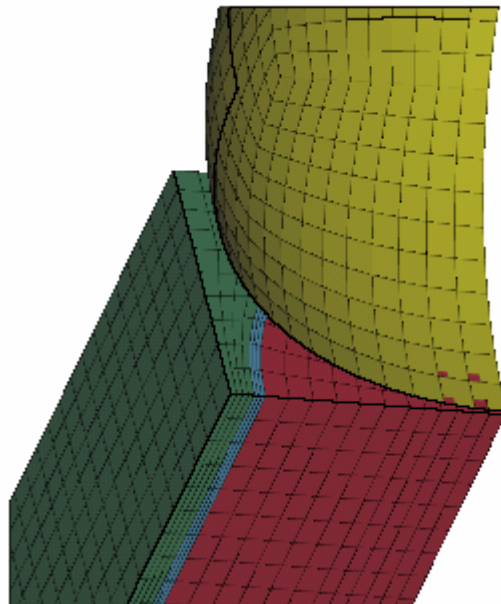Figure 4 Energies for a microindentation simulation.

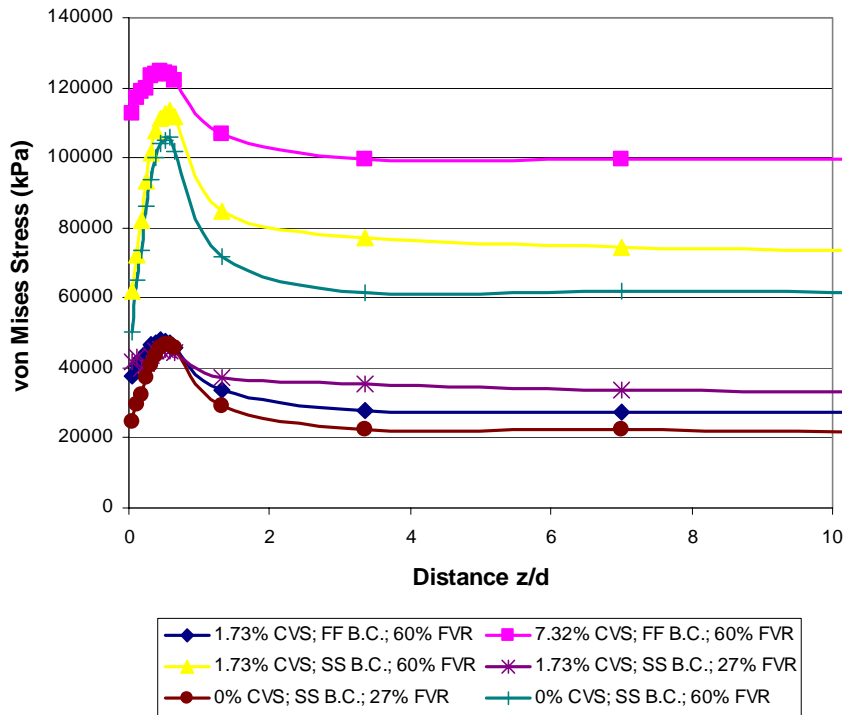Figure 5 Model of spherical indenter, fiber, interphase, and vinyl ester matrix

Figure 6 von Mises stress as a function of normalized distance from loading surface. (CVS = cure volume shrinkage; FF = free-free boundary condition; SS = symmetric-symmetric boundary condition)
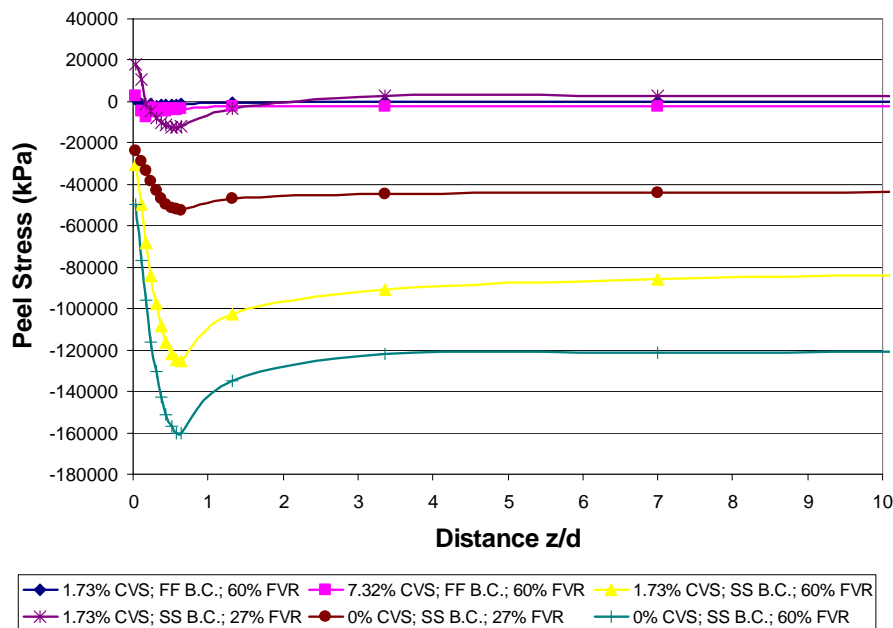

Figure 7 Peel stress between the fiber and interphase as a function of normalized distance from loading surface. (CVS = cure volume shrinkage; FF = free-free boundary condition; SS = symmetric-symmetric boundary condition)
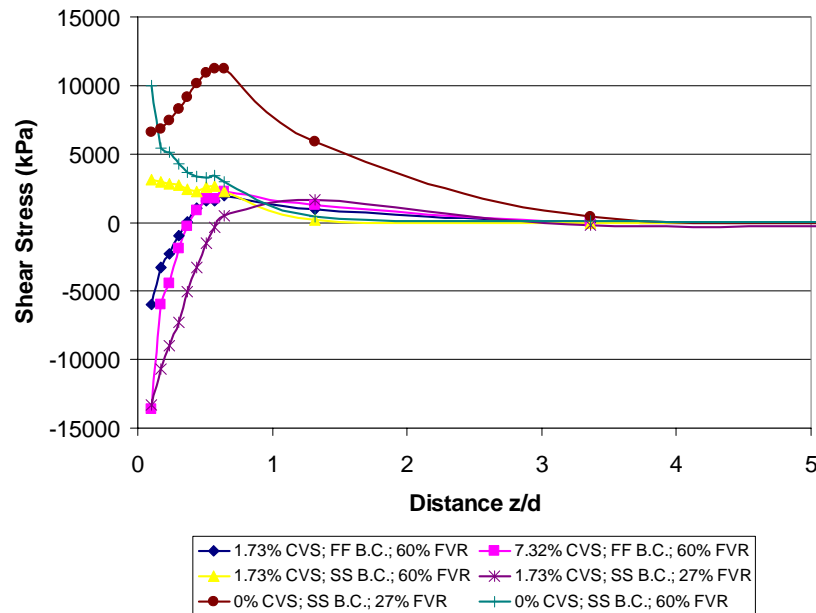
Figure 8 Shear stress between the fiber and interphase as a function of normalized distance from loading surface. (CVS = cure volume shrinkage; FF = free-free boundary condition; SS = symmetric-symmetric boundary condition)

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