

USING COMPUTATION FOR COMPOSITE MATRIX DEVELOPMENT

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ABSTRACT

Historically composite materials have been developed empirically rather than taking advantage of a relation between the macroscopic design-related mechanical performance metrics and the constituent material intrinsic atomic or molecular structure. Using computational techniques in a “virtual laboratory” sense would facilitate a more rapid development cycle and allow for increased interrogation of candidate materials. The method discussed is hierarchical rather than concurrent multi-scale simulation and relies on continuum analysis concept referred to as “Onset Theory” to provide the macroscopic guidance for the chemical simulation. This continuum method utilizes the deformation modes of dilatation and/or distortion and has been shown to provide insight into polymer behavior that can be related to microscopic interactions controlled by various bonded and non-bonded forces. The condensed matter physics insight into how deformation is influenced by these intra and intermolecular forces will be shown to be exploitable for matrix formulation purposes. We will show that computational tools such as Molecular Dynamics (MD) can be used as virtual formulation and with an appropriate protocol will yield results suitable for decisions leading to focused experiments and eventual composite evaluation demonstrating a performance improvement.

1. INTRODUCTION

1.1 Continuum to Discrete Connection

An empirical process rather than a systematic science-based approach that takes advantage of a relation between the end design related requirements and the constituent material atomic or molecular structural changes is extremely inefficient and usually unsuccessful. Connecting the discrete to continuum realms necessary for a physics based process could use a deformation based methodology that recognizes that modes of dilatation and/or distortion will provide new insight into polymer formulation. Coupling such a method to span the intersection between discrete and continuum descriptions of material behavior can be characterized as a hierarchical multi-scale approach that relies on new continuum analysis concept referred to as “Onset Theory”. Condensed matter physics provides additional insight in how each deformation mode is influenced by the intra and intermolecular forces within the polymeric binders. In addition a constraint to deformation provided by the high modulus fibers must also be considered when evaluating candidate matrix materials for suitability as a composite matrix. We will show that computational tools such as Molecular Dynamic (MD) simulation can be used as a virtual formulation aid, and with an appropriate protocol, will yield results suitable for informing

decisions leading to experiment and composite evaluation demonstrating a performance improvement.

1.2 Multiscale Modeling Concept

Recently, a continuum level physics based approach to numerical simulation of composite ultimate performance known as onset theory (formerly referred to as SIFT or the strain invariant failure theory)^{1,2} was reported. The theory represents composite performance through the use of strain invariants to describe the constituent material ultimate behavior. Onset theory based testing has shown that the matrix deformation behavior can have a profound effect on fiber performance and limit composite structure fiber dominated behavior. For example, testing shows that fiber performance is limited by the ability of the matrix to distort. Significant improvements in the performance of structural composites therefore depend upon the development of improved constituent materials, particularly improved resins.

Using computational methods coupled with experiment leads to a multi-scale methodology for composite matrix formulation that takes advantage of relations between composite performance, desired constituent bulk properties and the polymer matrix molecular structure. In order to perform the multi-scale development of new materials, the connection between the end-item and the constituent materials properties must be established. With the ability to express the structural performance in terms of a constituent material thermodynamic property, established structure-property relations and particle based computational methods to design new materials can be used.

Multi-scale materials modeling link continuum and atomistic methods and can be especially beneficial for applied development activities. It is critical that physically meaningful parameters are predicted and used in models for subsequent scales, avoiding the use of empiricism and fitting parameters. Multi-scale modeling is not reducible to a standard formula. Proper use will require uncovering the relationships of materials behavior responsible for a specific performance attribute, which remains an important focus of materials research. One possible approach that can be applied to many problems is to use chemical modeling and MD simulation to estimate bulk properties in an explicit manner and use the output to inform continuum simulation to predict performance at the component or system level.

1.3 Matrix Deformation Physics

Yield of amorphous polymers below the glass transition is a deviatoric or distortional deformation phenomenon. The variable yield stresses for various states of deformation and strain rates, rules out stress as a critical measure for the onset of irreversible behavior. It should be noted that while the critical values of stress vary widely with strain rate, the critical strain measures do not. The following criteria for the prediction of the onset of irreversible deformation within the matrix phase of a polymer-based composite system is proposed,

$$\mathcal{E}_{dilatational} = \mathcal{E}_1 + \mathcal{E}_2 + \mathcal{E}_3 \quad [1]$$

$$\varepsilon_{\text{distortional}} = \sqrt{\frac{1}{6}[(\varepsilon_1 - \varepsilon_2)^2 + (\varepsilon_1 - \varepsilon_3)^2 + (\varepsilon_2 - \varepsilon_3)^2]} \quad [2]$$

Where ε_i are the total (i.e. applied mechanical and thermal) microscopic principal strains in the matrix determined through micromechanical enhancement.³ The key materials development insight provided by onset theory is to consider a strain based deformation rather than a stress based approach to describing the molecular response to an applied mechanical load.

The two mechanisms correspond to the elastic and plastic processes occurring in matter under an applied stress. Forces applied to a physical system that result in a volume change are termed elastic and can be described using Hooke's Law. Volume expansion is a result of a local loss of intermolecular cohesion and a reduction of density. As long as the displacements are small, the linear restoring force or cohesive strength will reverse the effects on release of the applied force. These same cohesive forces also control the thermal expansion behavior and on cooling are due to the decrease in amplitude of the molecular vibrations. Plastic flow or a distortional process in a polymer is the result of highly localized atomic or molecular rearrangements which have been characterized as local deformation or shear transformation zones.⁴

Dilatation leading to cavitation at the molecular level involves separation of molecules against intermolecular attractive forces without the necessity to sever any primary backbone bonds, and the distortional process can occur without loss of intermolecular cohesion (at constant volume) in the polymer. The level of elastic dilatational expansion is directly relatable to the thermal contraction below the glass transition. In contrast, plastic response to an applied load is accommodated by intramolecular forces characterized by rearranging structural features such as bond bending and torsional rotation from an initially random orientation to one in line with the maximum principle strain. These key points provide the basis for our matrix development process.

1.4 Matrix Influence on Composite Properties

Additional relations linking a matrix property and a composite mechanical behavior exist that can be exploited to further expand the capability of molecular modeling as a predictive tool. For example the matrix modulus can be quantitatively related to the quasi-isotropic open hole compression strength. Testing to verify can be done with a single polymer-fiber combination and tested at several temperatures. Moisture absorption will negatively influence composite strengths especially in compression, using molecular modeling with cells containing water can be used to predict the decrease in modulus as a function of water content. Finally to determine equilibrium moisture content solvation free energy methods such as thermodynamic integration can be performed.

2. EXPERIMENTATION

Past composite materials development processes, rather than use a method informed by studies of polymer mechanical behavior, have instead adopted an empirical trial and error process as a method to determine success. Searching for the desired improvements defined in terms of the

end item rather than a constituent material property doesn't provide information regarding the influence of chemical structure that could be used for new matrix formulation schemes.

Defining a suite of new performance attributes for a new composite matrix resin require that a number of variables be considered. In addition to mechanical performance, the environmental stability and various manufacturing considerations must also be addressed. For aerospace, composite matrix materials are predominately epoxy resins cured with amine hardeners. The materials have a high percentage of aromatic structure and require curing at elevated temperature. The major considerations to be addressed when selecting ingredients for a new resin formulation include the strength and stiffness, high glass transition temperature, latent chemistry, fluid resistance and the ability to produce the uni-directional impregnated fiber product form (prepreg). An approach to intelligent formulation could include:

1. Computational generation of a combinatorial database: Select several potential diamine curatives and combine them with epoxies to produce a database consisting of matrix modulus, glass transition temperature, coefficient of thermal expansion, Poisson's ratio and uni-compression yield strain
2. Using the glass transition temperature and coefficient of thermal expansion, calculate the critical dilatational deformation for each simulated system. Using the compression yield strain, calculate the critical distortional deformation for each system
3. With a quantitative structure-property or informatics method, use the values calculated in #2 to generate a predictive model for the critical invariants
4. Use computational simulations to evaluate effects of off stoichiometric mixtures, variations in percent conversion and mixtures of more than two ingredients
5. Evaluate resin free energy of solvation for determination of fluid effects
6. For assessment of the amine reactivity, use quantum mechanics-based simulation in an indirect approach such as Fukui functions, or a direct approach by estimating the kinetic barriers from the computed reaction pathway and transition state
7. Various dynamic and static methods can be used to predict polymer elastic behavior.

2.1 Molecular Dynamic Simulation Methods

Use of MD as an aid to thermoset matrix formulation required the development of several new software tools and techniques. In particular, a robust and efficient workflow to simulate fully dense and equilibrated high glass transition temperature and high cross-link density epoxy resins; and subsequent analysis tools to extract values for the critical properties; such as the glass transition and the critical deformation measures of dilatation and distortion.

The accuracy of such simulations depend on two main aspects of the model, 1) the force field used to describe the interactions between atoms, and 2) the construction and evolution of atomistic structures that accurately represent the complex microstructure and topology of the material. The results reported here were obtained with the Schrödinger Materials Science Suite.⁵ The MS Suite is an integrated chemical simulation environment, with model builders, automated workflows, analysis and visualization capabilities, and quantum mechanics and MD-based simulation engines. All of the MD results discussed in this work was obtained using the GPU-enabled highly efficient Desmond MD engine.^{6,7} The force field used in these simulations corresponded to two commercial extensions of the well-known OPLS force fields: OPLS2005⁹ and OPLS3¹⁰. The cross-linked epoxy thermoset system was prepared using an automated

iterative bonding/MD equilibration process provided through the *Crosslink Polymers* module, starting from an initial equilibrated cell of reactive monomers constructed using the *Disordered System Builder* module. Thermophysical properties (e.g. T_g , CTE) and mechanical properties were computed using the *Thermophysical Properties* module, and *Elastic Properties* and *Stress-Strain Simulation* module, respectively. Molecular dynamics simulations of materials, are limited in size and atom count; our simulation cells contain a high conversion level thermoset, with a typical simulation cell of about 4 to 6 nm on the side.

3. RESULTS

The starting point is a well-equilibrated 3D condensed phase mixture of monomers of resin and curing agent: bisphenol-A epoxy (2,2-bis(4-glycidyloxyphenyl) propane, DGEBA) and 4,4 diamino diphenyl sulfone (44DDS). The DGEBA and 44DDS structures are shown in Figure 1, bottom and top, respectively. The cell of monomers was subjected to a simulated annealing protocol that included the application of pressure to compress the cell, and then fully relaxed using 40 ns NPT MD simulation giving a suitable final density, comparable to experiment. Next the reactant cell was “cured” automatically using an iterative MD approach with appropriate reaction sites identified. Structures of varying conversion were captured for subsequent analysis with the maximum extent of reaction reaching approximately 83%. Cells were selected from the range of cured structures annealed again followed by determination of thermophysical properties, elastic constants and a uni-compression loading to capture stress-strain response. Each of these evaluations generates information that can be related to composite performance.

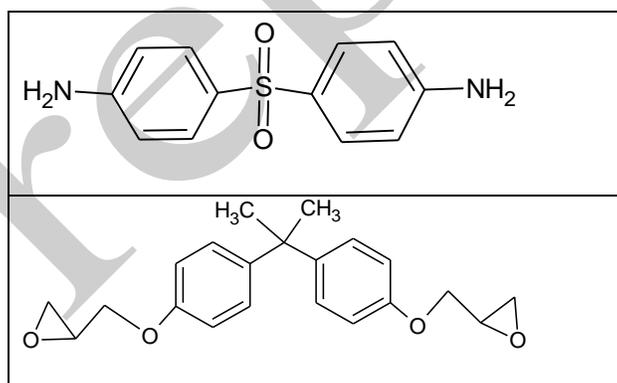


Figure 1. Molecular structures of 4,4-DDS and bisphenol-A epoxy (DGEBA)

3.1 Thermophysical Properties

To characterize phenomena involving volume changes we perform an isobaric volume vs temperature scan. The equilibrated periodic cell is heated to 800K and then stepwise cooling in 25° increments to $T=100$ K with a 5 ns NPT trajectory that equilibrates to a +/-5% density convergence. The cell dimensions and density are captured and reported. Figure 2 and 3 show

the specific volume as a function of temperature for a DGEBA/44DDS epoxy-amine system. The intercept of a linear fit to the data between glassy and rubber region or a hyperbola fit, similar to the method reported by Patrone *et al.*,¹¹ of the density vs temperature data is performed and taken as the glass transition temperature, T_g . The slope of the linear fit of glassy region is used as the thermal contraction behavior. The critical dilatational deformation at room temperature is calculated by determining the amount of volumetric contraction from the glass transition to a temperature of interest, usually room temperature (RT).

Table I, Comparison of estimated T_g with experiment

Fit method	T_g (K)	Volumetric CTE ($10^{-6}/K$)	J_1
Hyperbola	428	n/a	
Bilinear	426	159.64	.0246
Experiment ¹²	441		

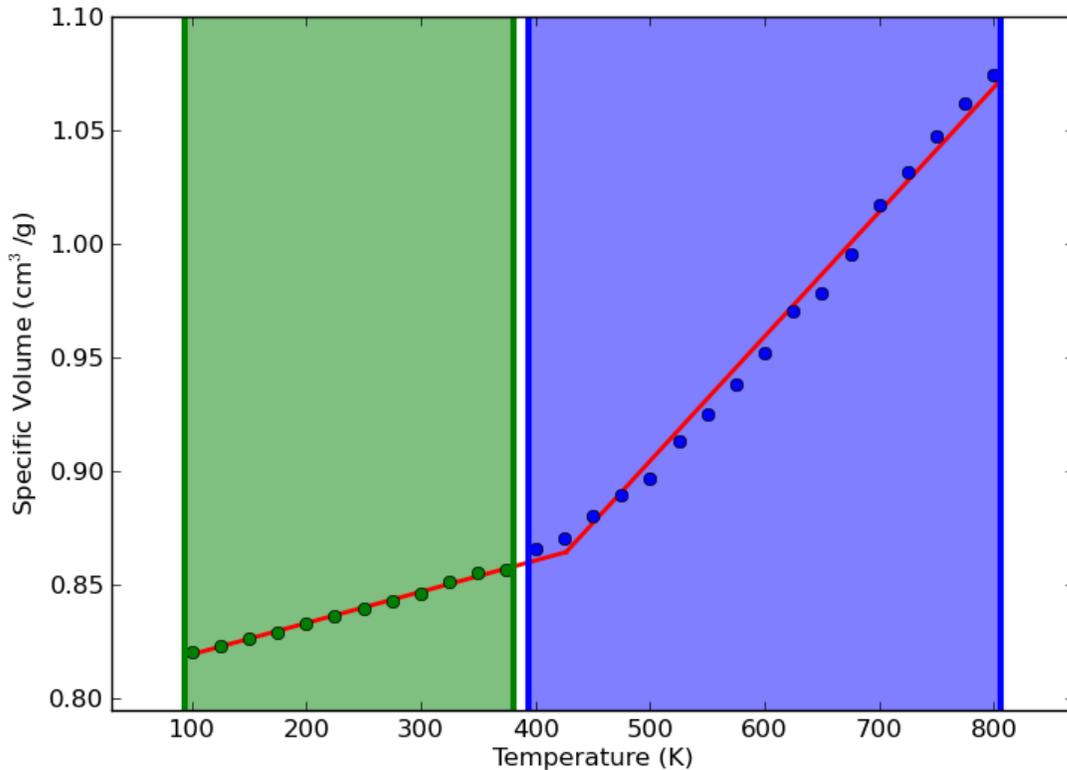


Figure 2. Specific volume vs Temperature for DGEBA/44DDS system with the results of the bilinear fit shown.

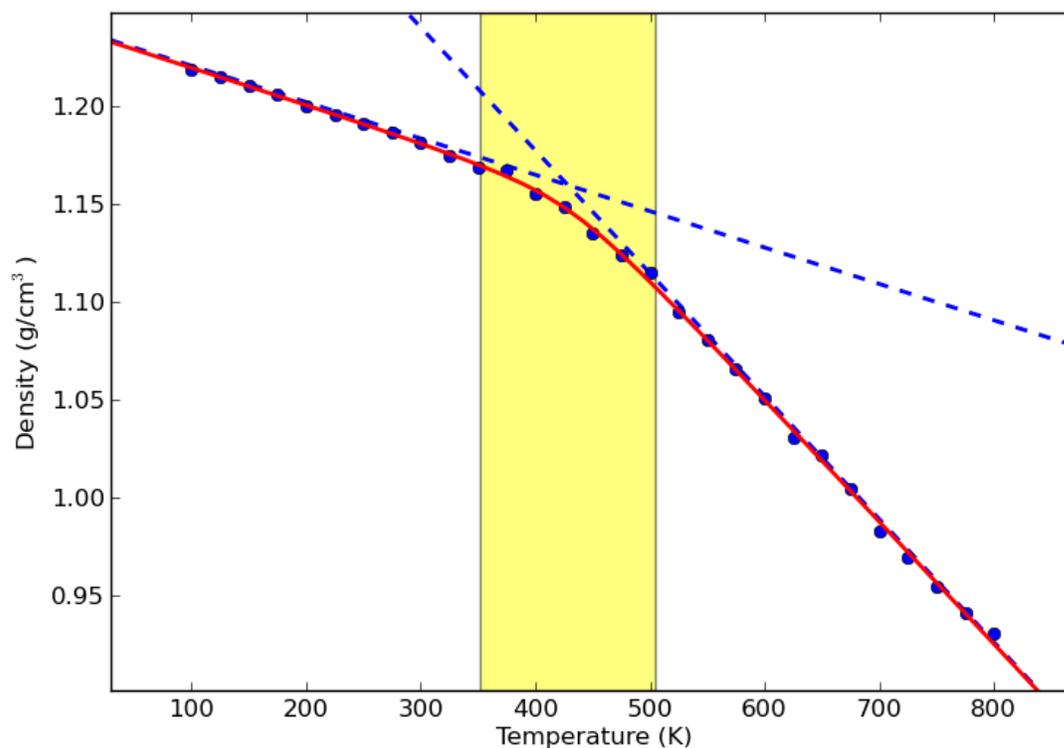


Figure 3. Density vs Temperature for DGEBA/44DDS system with the results of the hyperbola fit shown.

It should be noted that reported experimental T_g 's will depend on the curing conditions as well as the method of measurement and data analysis. The analysis approach will most likely depend on the interests of the investigator. For those concerned with elevated temperature mechanical performance, the onset of the modulus vs temperature drop will of importance and correlates well with the data shown in figures 2 and 3. $\tan \delta$ or loss modulus peaks trend to higher temperatures.

3.2 Elastic Constants

Matrix modulus will have direct bearing on the composite compression strength. Observation of composite compression test results at various temperatures confirms the influence of the matrix modulus. Simulation of elastic constants can be performed at several temperatures and be used to determine the reduction in composite performance with temperature. Simulation cells can also be constructed with included water molecules to determine the reduction due to the presence of a small molecule penetrant.

To illustrate the use of atomistic simulation to estimate the matrix modulus of the DGEBA/44DDS thermoset, the stress-strain response was calculated for the system using a

direct method. Using this direct static approach, the Lamé coefficients (μ , λ) can be estimated giving a path to the moduli and Poisson ratio for the system.¹³ This method entails constructing and minimizing a series of deformed cells in both the positive and negative direction by a set delta; $\delta=0.002$ (up to +/- 0.04). The uniaxial tension (C_{11} , C_{22} , C_{33}), pure shear (C_{44} , C_{55} , C_{66}), biaxial tension (C_{12} , C_{13} , C_{23}), and bulk compression deformations were generated and minimized. Each subsequent deformation is based off the last minimized deformed cell. To capture the dynamic nature, 10 snapshots at 100 ps intervals were taken from a 1 ns MD trajectory (NPT, 1 atm, 300 K). Each snapshot was subjected to the above deformations and the final modulus and Poisson ratio were computed. The properties reported in Table II are a weighted average based on the Boltzmann distribution of the minimized non-deformed cell energy.

Table II, Computed and experimental modulus and Poisson ratio

	Young's Modulus (MPa)	Poisson Ratio
OPLS3	3195	0.25
Experiment	3571	N/A

3.3 Uniaxial Compression/Tension Testing

Distortional deformation is a mechanism that involves a shape change without undergoing a volume change. The distortional capability of a polymer network involves the ability of the molecular backbone to rotate through dihedral angles. These rotations increase the ability of the system to absorb strain energy by means of a dissipative process. During deformation there is an increase in polymer backbone torsional transitions through rotation of dihedral angles and that the percolation of this mobility leads to the yield event. These torsional rearrangements are dissipative events that are responsible for the non-linear stress-strain response. The critical distortional event represents the maximum level of torsional rearrangement before the onset of flow or the complete disappearance of local energy minimums due to the relaxation to new local minimums.

To evaluate the stress-strain response of the system under volumetric constraints, a series of NVT simulations are carried out in an automatic fashion, distorting the cell according to the protocol reported by Strachan and co-workers,¹⁴ setting the $\Delta\epsilon_1 = 0.015$, $e_2 = e_3 = L(1-(1+e_1)^{-\zeta})$; $\zeta=0.5$ for volume conserving uniaxial deformation. Yield in this instance is defined as the strain at maximum applied stress.

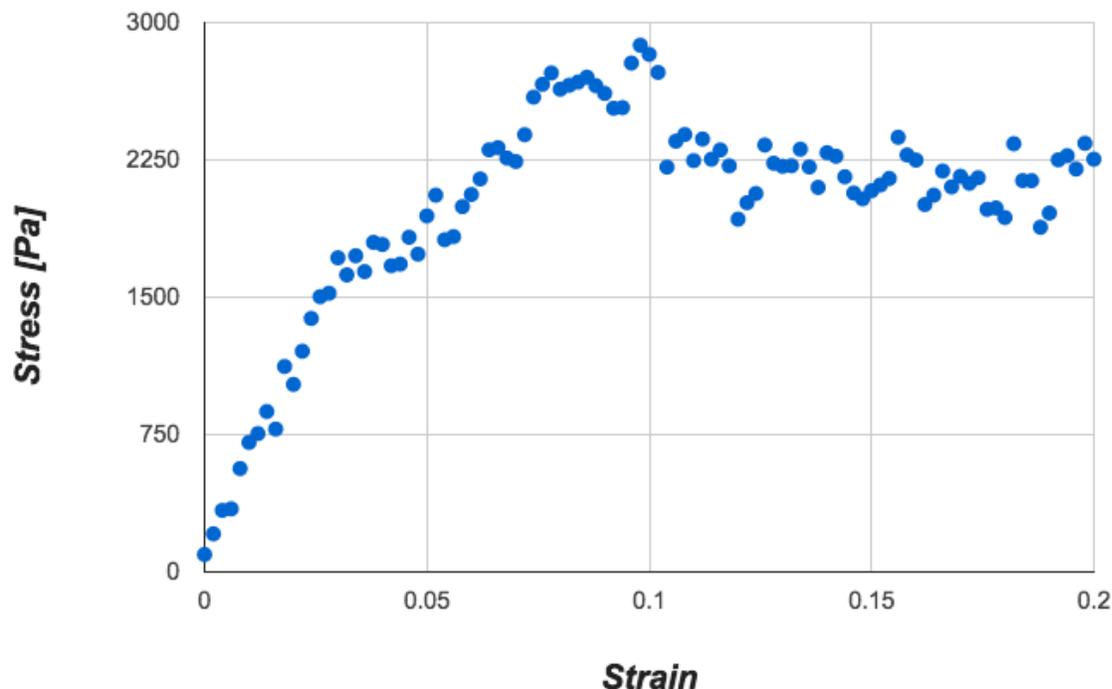


Figure 4. Sample stress-strain curve (effective stress vs. distortional strain, $\epsilon_{\text{distortional}}$) for DGEBA/44DDS.

The value considered as critical is taken to be the strain at the yield stress defined as the stress at zero slope for the stress-strain relation. For the DGEBA/44DDS system the critical distortional strain would be approximately 0.09.

4. CONCLUSIONS

Assessment of the simulation method is provided in the comparison of the simulation prediction for glass transition with experiment. In this work, the MD simulations were carried out with Desmond, a highly optimized and efficient general purpose MD program able to run on graphical processing unit (GPU) cards, giving a speed-up of more than 100 times over execution on CPU. The throughput of Desmond on GPU for chemical systems of ca. 50K atoms is more than 170 ns/day, greatly increasing the potential impact of atomistic modeling and MD simulation on advanced composite development. With adequate high performance computing resources, a decrease in research time necessary to generate sufficient data for decisions can be reduced by up to twentyfold. The time and cost savings can be used to evaluate many more iterations of a formulation strategy. The dramatic visualization insight afforded by computational analysis also contributes to a rapid advancement to an optimal solution. The simulation of a polymer being considered as a potential new composite matrix using an onset theory approach can yield the information necessary to determine performance when combined with the fiber reinforcement. The critical invariants have been used to predict ultimate performance of various mechanical test coupon types including configurations used to determine design values. For example the relation between polymer modulus and compression performance has been established. Onset theory

recognizes that thermal and mechanical expansion have the same atomistic origin so simulation of the thermal expansion will allow prediction of a critical mechanical expansion. Deviatoric response can also be determined when it is recognized that local deformation beyond yield will be restrained by the fibers within a composite and flow will be prevented. Therefore yield by way of a distortion represents a critical process and will result in a cavitation due to limiting macroscopic flow.

5. ACKNOWLEDGEMENTS

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