Available online at www.sciencedirect.com

ScienceDirect

Scripta Materialia 70 (2014) 18–24

Scripta MATERIALIA

www.elsevier.com/locate/scriptamat

Viewpoint Paper

Computational formulation of a new composite matrix

S. Christensen[a,*] and R. D'Oyen[b]

[a] *Boeing Research & Technology, Seattle, WA 98124, USA*
[b] *Mechanical Engineering Directorate, Raytheon Co., Sudbury, MA 01776, USA*

Available online 25 September 2013

Abstract—Using computational methods and experiments, we have established a methodology for the prediction of composite performance that allows materials development by design. The method is demonstrated with a matrix formulation development that validates the relations we have established between composite performance and constituent properties. The use of molecular dynamics for thermoset matrix formulation required the development of several new techniques. Our results show that composite performance is predictable and improvements are achievable through the proper selection of resin components.

Keywords: Composites; Matrix; Molecular dynamics; Epoxy

1. Introduction

Composite materials consisting of organic polymer resins and high strength and stiffness carbon fibers have undergone significant changes over the last 40 years. The performance improvements have been primarily due to increases in fiber strength and stiffness. The improvement in performance realized over the last 20 years has been primarily due to the introduction of high strength intermediate modulus fibers and with associated matrix formulation enhancements. These materials represent the state of the art for aerospace structural applications, including the Boeing 787. This illustrates the need for the materials development community to have visibility into the analysis and design of composite structures. Composite design should include an assessment of the onset of irreversible deformation and, in some cases, the ultimate capability of the structure. Within the aerospace industry mechanical performance criteria are usually addressed through empirical point-design methods that require extensive testing. Failure criteria designed to help alleviate this testing requirement are usually dependent on empirical curve-fitting. A failure theory that would apply to the general condition must utilize intrinsic critical material properties that describe the onset of irreversible deformation for all possible loading conditions, boundary conditions and geometric structural configurations.

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] has provided insight into the constituent material behavior necessary for optimal composite performance. The theory represents composite performance through the use of strain invariants to describe the constituent material ultimate behavior. Despite the advances enabled by an onset theory-based structural design method, the performance of composite structures is still ultimately limited by the characteristics of the constituent materials. For example, our 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 we have established a multi-scale methodology for new composite matrix formulation development that takes advantage of relations we have discovered between composite performance, the 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 known. For example, a typical aerospace design value is a quantity called open hole compression strength. The

* Corresponding author. Tel.: +1 12065444677; e-mail: stephen.christensen@boeing.com

1359-6462/$ - see front matter © 2013 Published by Elsevier Ltd. on behalf of Acta Materialia Inc.
http://dx.doi.org/10.1016/j.scriptamat.2013.09.017

structural variables for the test include the ply orientation, size of the hole with respect to the width of the test specimen, specimen buckling support including the specimen thickness and test conditions such as temperature, rate of loading and other potential adverse exposure conditions. With the ability to express the structural performance in terms of a constituent material thermodynamic property, we can now use established structure–property relations and particle-based computational methods to design new materials. As an example, we will show how we couple the molecular dynamics component of a hierarchical multi-scale simulation approach for understanding materials behavior with the continuum level analysis insight.

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. With the use of computational tools it is envisioned that new materials could now be developed within the design cycle of a new product. 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 molecular dynamics to simulate bulk properties in an atomistically explicit manner and use the output to inform a continuum simulation method to predict performance at the coupon through airplane level. The overall computational approach is shown in Figure 1. The essential feature, described above, is indicated by the molecular/continuum interface representing the thermodynamic connection between the levels of analysis. Our studies conclusively identify that a deformation or strain-based rather than a stress-based model be used to translate the continuum level performance into molecular level characteristics.

Yield within glassy polymers is a deviatoric or distortional deformation dominant phenomenon but they can deform irreversibly due to dilatational dominant behavior [2]. In addition, it is well known that polymer deformation is sensitive to the hydrostatic component of stress. The physically inconsistent yield stresses for various states of deformation and strain rates rule out stress as a critical measure for the onset of irreversible behavior because of the polymer viscoelastic behavior. It should be noted that, while the critical values of stress

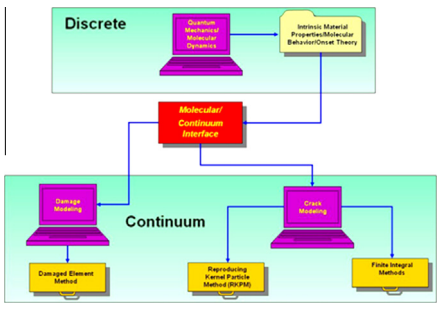

Figure 1. Organization of a heirarchical multi-scale modeling approach.

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 glassy polymer-based composite systems are proposed:

$$\varepsilon_{dilatational} = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 \quad (1)$$

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

where $\varepsilon_{dilatational}$ is the critical dilatational strain, $\varepsilon_{distortional}$ is the critical distortional deformation and ε_i are the total (i.e. applied mechanical and thermal) microscopic principal strains in the matrix phase determined through micromechanical enhancement. 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 deformation of matter can be divided into two categories: dilatation (or volume expansion) and distortion (or deviatoric). The mechanisms correspond to the elastic and plastic processes occurring in matter under a uniform state of stress. Forces applied to a physical system that result in a volume change are termed elastic and have been adequately 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. The cohesive forces in question are also responsible for the thermal contraction with temperature and a direct consequence of the decrease in amplitude of the molecular vibrations as the polymer is cooled. Plastic flow or distortional processes in atomic or molecular materials is usually the result of highly localized atomic or molecular rearrangements which have been characterized as local deformation or shear transformation zones.

Baljon and Robbins [3] performed molecular modeling of an L–J solid between constraining surfaces and their results demonstrate that the initial elastic response is governed by the inter-particle attraction; yielding is evidenced by a cavitation event with the density decreasing during the elastic deformation. In their model they note that when the cavities form on yielding, the rest of the material returns to the equilibrium density and the force on the separating walls drops sharply. Further separation causes plastic flow in a sequence of discrete yield events with nearly elastic behavior between the events. The cavity sizes increase at each yield event, eventually coalescing, with the ultimate event being complete severing of the material. Even though their model does not contain the bonded connectivity of a polymer, they note that two invariant scalars can be used to describe the amount of dilation and shear stress on a system in agreement with the general explanation of deformation as either dilation or distortion embraced by the onset theory adopted methodology.

Malandro and Lacks [4] investigated the mechanisms of deformation from an "inherent structures" viewpoint and provide a link between the macroscopic observations and microscopic mechanisms in their explanation