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Prediction of the chemical and thermal shrinkage in a thermoset polymer

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ABSTRACT

A multi-scale model for the response of a bi-material “thermostat”, consisting of a single unidirectional lamina of carbon/epoxy and an uncured layer of neat diglycidyl ether of bisphenol F (DGEBF) with curing agent, diethyltoluenediamine (DETDA), is developed in order to measure thermal strains during a prescribed, but arbitrary thermal history. Molecular modeling simulations provided the elastic modulus, coefficient of thermal expansion, glass transition temperature of DGEBF/DETDA as a function of degree of cure. Cure kinetic properties were determined with differential scanning calorimeter measurements. The model allowed separation of strains due to cure shrinkage and thermal expansion. Combining the molecular modeling predictions, cure kinetic measurements and “thermostat” deflection measurements, the complete polymer shrinkage phenomenon is determined over a prescribed thermal cycle. Furthermore, this work can provide a vehicle to develop cure cycles wherein the difference between instantaneous glass transition temperature and specimen temperature is controlled to provide optimum cure cycles for minimum cure shrinkage.

1. Introduction

Shrinkage in thermosetting polymers can be a source of residual stresses in fiber-reinforced composites due to the mismatch in thermal expansion coefficients between fiber and polymer matrix and due to the chemical shrinkage which occurs during the cross-linking reaction of the polymer matrix. Measurement of cure shrinkage can be difficult since the thermal history of a typical cure cycle excites the two phenomena simultaneously. Further, several thermoset polymers are liquids at ambient temperature and present experimental difficulties in using conventional measurement techniques such as dilatometry. One approach to measuring polymer matrix shrinkage during cure is the bi-material “thermostat”, first analyzed by Timoshenko [1], wherein two materials with differential shrinkage are joined together and subjected to a temperature change [2–6]. The resulting curvature (or deflection) can be used to measure the difference in shrinkage of the two materials, but only if the Young’s moduli and glass transition temperatures of the two materials are known. However, measuring these properties of the matrix polymer can be difficult and expensive to accomplish. Further, the recent development of molecular modeling techniques for prediction of thermoset polymers as a function of degree of cure (DOC) provides a direct way to predict these polymer properties in a quasi-static, temperature-dependent form. Time dependence is not predicted by molecular modeling since the time frame for the molecular simulations is quite different from the testing conditions. Hence, the molecular modeling predictions can be used only as values of specific properties as a function of the instantaneous value of degree of cure. Multi-scale modeling that is based on the results of molecular dynamics simulation offers a reduction of experimental work necessary for material characterization. However, time scale limitations that exist for molecular dynamics simulation require certain assumptions to be established to ensure the connection between conditions implemented in the simulation and the thermoset processing condition due to the known time and rate dependent response of thermosets. This includes a shift in glass transition temperature for thermosetting epoxies within the generally accepted range of 3–5 K per order-of-magnitude difference between the cooling rate during the test and the simulation [7,8], although the value of shift may be a function of molecular weight. Never the less, this process provides an approach to provide the necessary polymer properties by the molecular modeling for the multi-scale simulations.

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In the following, the authors describe an approach for combining molecular model predictions of polymer properties as a function of degree of cure with experiments to isolate the shrinkage characteristics of the polymer from its thermal expansion during an arbitrary thermal history. The molecular modeling approach for determining the Young's modulus, coefficient of thermal expansion (CTE), chemical shrinakge and glass transition temperature of diglycidyl ether of bisphenol F (DGEBF), with curing agent, diethyltoluenediamine (DETDA), versus degree of cure is described. Next, the cure kinetic properties, developed by Differential Scanning Calorimetry (DSC) are presented. A modified beam theory for the bi-material "thermostat" with variable material properties as a function of DOC is developed to relate "thermostat" curvature to shrinkage of the polymer due to both chemical shrinkage and thermal expansion. Combining the molecular modeling predictions, cure kinetic measurements and "thermostat" deflection measurements, the complete polymer shrinkage phenomenon is determined over a prescribed thermal cycle.

2. Molecular dynamics (MD) modeling

The thermo-mechanical properties of the thermoset polymer as a function of degree of cure, required to inform the continuum "thermostat" model, were obtained from molecular dynamics simulations. The following describes the atomistic simulations of the process of curing using the MD-based polymerization simulator (MDPoS) method developed in recent years [8–13]. Fig. 1 illustrates the primary reaction of an epoxide group at the end of the DGEBF monomer with an amine group on the DETDA. Each amine group can react with two epoxy monomers and the chemical reaction during cure leads to a three dimensional amorphous network. The model system consisted of 256 DGEBF monomers and 128 DETDA molecules. Such a system with ideal stoichiometry could, in principle, lead to 100% conversion, i.e., complete reaction of all sites. The total number of atoms in this initial model system was 16,000. The open source MD package LAMMPS [14] with the Dreiding molecular force field [15] was used in all of the simulations.

The MD-based polymerization simulator (MDPoS) method was used to mimic the curing process of thermoset polymers [9] and to obtain polymer samples with various degrees of cure for the subsequent MD simulations. MDPoS consists of three main stages (see flowchart shown in Fig. 2) briefly described in the following. The details can be found in Ref. [9]:

(1) Pre-crosslinking: the initial stage packs and equilibrates a mixture of the epoxy and curing agent with the desired stoichiometry into a simulation cell with three-dimensional periodic boundary conditions. A system was initially created at low density (e.g., 0.5 g/cm^3) and relaxed by energy minimization using a conjugate gradients method and then thermalized, using an isothermal and isochoric (NVT ensemble) MD simulation for 50 ps at 600 K followed by an isothermal, isobaric (NPT) MD simulation for 400 ps at atmospheric pressure to fully equilibrate the initial mixture before chemical reactions were started.

(2) Crosslinking: the second stage involved curing the system. Here the chemical reactions were simulated in a stepwise manner using a distance-based criterion. Bonds were created between reactive atoms within a cutoff distance normally taken as four times the equilibrium N–C bond length (1.41 Å). New bonds were turned on slowly using a 50 ps long multi-step relaxation procedure to avoid large atomic forces. After the new bonds were fully relaxed a NPT simulation for an additional 50 ps was performed before the new set of bond creations was attempted. All these simulations were carried out at $T = 600$ K and the cycles of chemical reactions followed by thermalization were repeated until the desired DOC was achieved.

(3) Annealing: samples with various degrees of cure were cooled to room temperature to obtain properties as a function of temperature and degree of cure. The polymer samples were cooled down to room temperature in a stepwise manner with rates between 10 K/60 ps and 10 K/200 ps. The annealing process was used to predict the glass transition temperature, T_g, and the coefficients of thermal expansion above and below T_g.

The T_g was computed for the polymer from the change in slope of the density–temperature relationship during cooling at constant

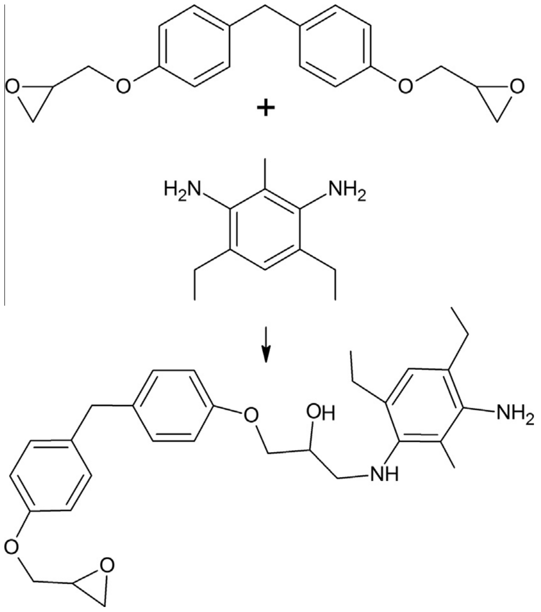

Fig. 1. Molecular structures of a DGEBF monomer, a DETDA and the primary reaction of a DGEBF monomer with a DETDA.

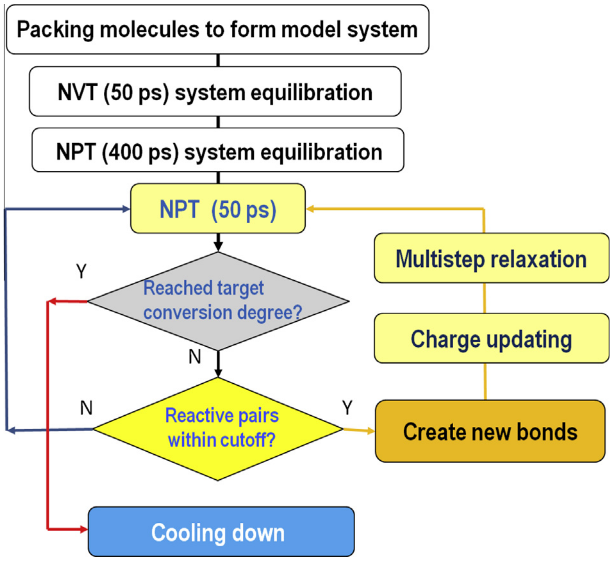

Fig. 2. Flowchart of curing process simulation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)