Molecular dynamics simulations on cyclic deformation of an epoxy thermoset

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ABSTRACT

We use molecular dynamics simulations to study the thermo-mechanical response of a thermosetting polymer (diglycidyl ether of bisphenol A with 3,3′diamino-Diphenylsulfone) subject to cyclic loading for a family of tri-axial deformation paths and two different load levels and strain rates. We focus on how the relative amount of deviatoric and volumetric deformation affects strain accumulation and energy dissipation and find that uniaxial stress conditions lead to the highest rate of strain accumulation and dissipation. A characterization of the molecular-level processes responsible for strain accumulation provides insight into the observed role of volumetric and deviatoric deformations and explains the relatively low strain accumulation for purely deviatoric or volumetric loads. These results may help the design of polymer matrix composites with improved performance under cyclic loading conditions.

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1. Introduction

Polymer matrix composites (PMCs) are extensively used in aeronautical and automotive industries. Currently, these applications have a demand of 10–50 years lifetime for important PMC structural components, which are inevitably subjected to cyclic loading. Other important applications such as electronics and microsystems also involve periodic loading. The time dependence of the mechanical properties of PMC is dominated by the hereditary nature of its amorphous polymer matrices, i.e. viscoelasticity [1]. The design of new PMC formulations and the optimal use of existing ones would benefit from an in-depth understanding of how polymers behave under a variety of time-dependent loading conditions. A further challenge in polymer composites is that the matrix experiences complex, multi-axial loading due to the mechanical constrains imposed by the relatively stiff fibers. Among possible polymeric matrices, thermosets are commonly used in structural applications due to their high stiffness and strength as well as excellent creep and thermal resistance. Therefore, this paper uses molecular dynamics (MD) to characterize the response of an amorphous thermoset polymer subject to cyclic loading for a family of loading pathways involving varying amounts of deviatoric and volumetric deformation. We focus on a thermoset resulting from the epoxy resin diglycidyl ether of bisphenol A

(DGEBA, known commercially as EPON 825) with the curing agent 3,3′diamino-Diphenylsulfone (33DDS).

When a material is subject to a primary static load plus a secondary cyclic load over an extended period of time strain accumulation occurs even if the load is significantly below the yield stress. The cyclic accumulation of plastic strain, also known as ratcheting effect or cyclic creep, contributes to the fatigue failure of materials. Various loading factors such as stress level, stress rate, and loading path have been extensively studied in the last several decades; see, for example, the critical reviews by Ohno [2,3] and Kang [4]. The following observations apply generally for all materials when subjected to cyclic loads: i) the ratcheting strain gradually increases cycle by cycle and progresses faster with higher mean-stress level and/or larger stress amplitude; ii) the ratcheting strain per cycle is strongly rate-dependent and tends to be larger with decreasing strain rate; iii) multiaxial ratcheting is lower than the uniaxial one under plastically equivalent loading conditions. However, a systematic understanding of how multi-axial loads affect strain accumulation and an explanation of such behavior in terms of molecular processes are still not available. Such knowledge would be important to understand material-specific ratcheting and the multi-axial loads present in polymer matrix composites. For example, the ratcheting strain rate decreases cycle by cycle and even completely stops for some cyclic hardening materials such as stainless steel [5] but increases for cyclic softening materials [6,7].

As compared to metals, strain accumulation in polymers exhibit complexities that originate from its molecular nature, including complex history dependence, density changes, and temperature

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excursions comparable to their quench depth (difference between glass transition and operating temperatures). Different from metals, polymers typically experience a hysteresis and cyclic softening when a critical cyclic strain is attained [8]. Rabinowitz and Beardmore [9] experimentally studied the stress–strain behavior of a wide variety of glassy polymers under uniaxial strain-controlling cyclic loading. They observed continuously cyclic softening for ductile polymers (polycarbonate (PC) at room temperature) but slight softening for semi-ductile polymers (poly-methylmethacrylate (PMMA) at room temperature). Rittel [10] investigated hysteretic heating on PMMA and PC subjected to cyclic compressive loading and characterized heating upon cycling observing maximum temperatures reaching close to the glass transition temperature. The reduced yield strength caused by the increase in temperature has an impact on the failure mechanism and fatigue life of polymers under cyclic loadings. Meyer and Pruitt [11] examined the role of cyclic strain on the high molecular weight polyethylene (PE) and found not only cyclic softening but also density reduction. Hizoum et al. [12] recently conducted cyclic uniaxial tension and retraction tests on high-density PE and reported that the accumulation of nanovoids resulted from small-strain cyclic loading causing softening. Dorado and Christiansen [13] studied the annealing effect on the elastoplastic property of a semicrystalline polymer by performing cyclic tension tests and concluded that annealing at relatively higher temperatures is very helpful in reducing ratcheting rate and delaying necking occurrence. Liu et al. [14] experimentally investigated the evolution of ratcheting strain of PMMA at different temperatures and stress levels and found that the ratcheting strain rate increases with increasing temperature or higher stress level. Zhang and Chen [15] conducted a series of multiple step multiaxial ratcheting experiments on polytetrafluoro-ethylene (PTFE) and found multiaxial ratcheting is sensitive to the loading history. Specifically, prior cycling at high stress and amplitude or low strain rate significantly limits the ratcheting strain of subsequent cycling at a different level.

Relatively fewer studies have been conducted on thermosets. Isayev et al. [16] measured dynamic properties (mainly dynamic shear modulus) of crosslinked epoxy resin (Epon826 with diethylenetriamine) under torsional cyclic deformation and found cyclic softening. Shen et al. [17,18] performed uniaxial cyclic tests on an epoxy resin (Epon826 with Epicure 9551) and found that the stiffness reduction was very small and the ratcheting strain rate decreases with increased number of cycles and tends to zero after ∼300 cycles, which means there is an asymptotic value for the ratcheting strain. They also found that the ratcheting strains under various testing conditions are fully viscoelastic. Tao and Xia [19] also studied the ratcheting of the same epoxy resin (Epon826 with Epicure 9551) under stress-controlled uniaxial loading and investigated its effect on fatigue life. They concluded that the ratcheting strain is mainly recoverable viscoelastic deformation and the accumulation of ratcheting strain had little detrimental effect on the fatigue life, compared with strain-controlled fatigue test results.

Molecular simulations are playing an increasingly important role in the characterization of thermo-mechanical properties of polymers and contributing our understanding of these materials; see, for example, Refs. [20–22]. However, atomistic simulations of polymers under cyclic loading are scarce. Yashiro et al. [23–25] conducted molecular dynamics simulations on PE and poly-butadiene (PB) under cyclic loading using a united atom force field and found that the polymer chains tend to align with the loading axis. In this paper, we use all-atom MD simulations to study ratcheting effect of a thermoset of DGEBA/33DDS. The objective is to investigate the effects of stress level, loading rate and loading path, on the ratcheting strain and characterize the molecular processes associated with cyclic deformation of thermoset polymers. We focus on the role of the relative amount of volumetric and deviatoric stress on inelastic deformation; molecular simulations have shed light into this problem but only for monotonic loading [26–28].

2. Simulation details and analysis

2.1. DGEBA/33DDS and crosslinking procedure

Epoxy resin DGEBA can react with a full range of curing agents. The DGEBA/33DDS system chosen for this study exhibits all the important thermo-mechanical properties of commercial epoxy resins and a more direct comparison between molecular simulations and experiments can be done because its relative compositional simplicity. We employ the general-purpose Dreiding force field [29] with harmonic covalent terms in all our MD simulations and non-bond van der Waals interactions are described with Lenard–Jones 6–12 (LJ) potential function during the crosslinking process and via the Buckingham potential with exponential repulsion and power 6 attraction (X6) for the prediction of thermo-mechanical properties. Partial atomic charges on DGEBA/33DDS are calculated using the self-consistent electronegativity equalization method as described by Gasteiger [30]; these atomic charges are updated for the atoms involved in the chemical reactions during curing process [31].

We recently developed a molecular modeling procedure, the MD-based polymerization simulator (MDPoS), to simulate the curing process of thermosets. The details of this approach are described in Ref. [31] and a brief overview of the key steps is provided below. The simulation begins with a mixture of DGEBA monomers and 33DDS molecules with the desired stoichiometry into a simulation cell. Fig. 1 shows the molecular structures of monomers DGEBA and 33DDS with the reactive sites are highlighted in red. We use the "activated" DGEBA, shown in Fig. 1(b), as the starting resin configuration. The unreacted mixture is equilibrated using MD simulations under constant temperature and volume conditions (NVT ensemble) followed by an isothermal, isobaric (NPT conditions) simulations for enough time (50 ps NVT and 400 ps NPT in this study) to let the liquid reach equilibrium.
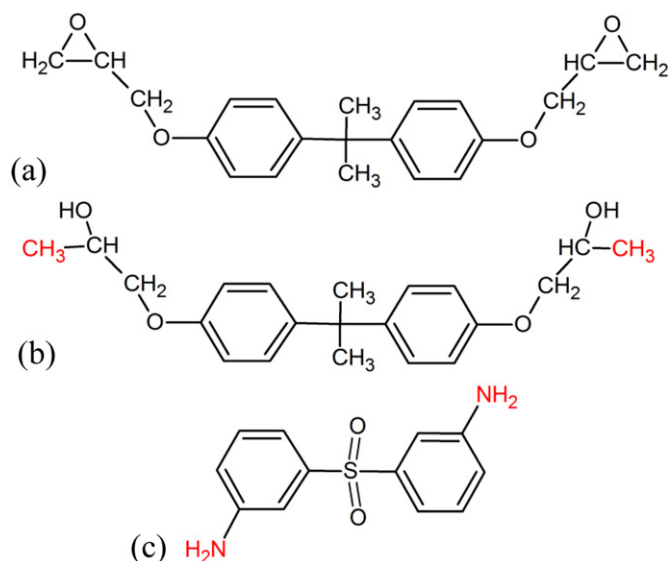

Fig. 1. Molecular structures of (a) DGEBA, (b) activated DGEBA and (c) 33DDS.