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Toward the constitutive modeling of epoxy matrix: Temperature-accelerated quasi-static molecular simulations consistent with the experimental test

Hyungbum Park[a], Joonmyung Choi[a,b], Byungjo Kim[a], Seunghwa Yang[c], Hyunseong Shin[a,b], Maenghyo Cho[a,b,*]

[a] Division of Multiscale Mechanical Design, School of Mechanical and Aerospace Engineering, Seoul National University, Republic of Korea
[b] Institute of Advanced Machines and Design, Seoul National University, San 56-1, Shillim-Dong, Kwanak-Ku, Seoul 151-744, Republic of Korea
[c] School of Energy Systems Engineering, Chung-Ang University, Seoul 156-756, Republic of Korea

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ABSTRACT

We propose an efficient simulation-based methodology to characterize the quasi-static (experimental low strain rate) yield stress of an amorphous thermoset polymer, which has generally been considered a limitation of molecular dynamics (MD) simulations owing to the extremely short time steps involved. In an effort to overcome this limitation, the temperature-accelerated method – in which temperature is treated as being equivalent to time in deformation kinetics – is employed to explore the experimental strain rate conditions. The mechanical tensile behavior of a highly crosslinked polymer is then investigated with MD simulations by considering different strain rates and temperatures below the glass transition temperature. The derived yield stress represents the time- and temperature-dependent characteristics, showing that the yield stress decreases with increasing temperature and decreasing strain rate. Changeable vertical and horizontal shift factors are introduced for the first time to reflect nonlinear characteristics of the yield stress across a broad range of strain rates and to quantify the correlation between increasing temperatures and decreasing strain rates. With the proposed method, the Eyring plot, which describes the rate effect on yield from quasi-static to high-rate conditions, is predicted from MD simulations, and agrees well with macroscopic experimental results. From the constructed Eyring plot, the experimentally validated quasi-static stress-strain response is also estimated by using linear elastic model and Ludwick's hardening model. The proposed method provides new avenues for the design of glassy polymers using only fully atomistic MD simulations, thus overcoming the existing temporal scale limitations.

1. Introduction

Owing to the unique crosslinked molecular network structures between polymer chains, amorphous thermoset polymers have been widely used in various applications that require high performance, light weight, and structural robustness. Since the macroscopic properties – such as elastic modulus, yield strength, toughness, and the glass transition temperature – can be readily tailored by adjusting microscopic parameters (including the molecular structure of resin and crosslinker, molecular weight, conversion ratio, etc.), thermoset polymers currently attract significant interest in industries that rely on advanced materials and high-performance polymers [1–5].

Among various thermoset polymers, epoxy is the most widely used one – not only as an independent functional material, but also as a host matrix for composites and nanocomposites [6–8]. Because of the recent advances in computational methods, which can be applied for modeling condensed matter, theoretical simulations of epoxy polymers have been recently performed by using various molecular mechanics [9,10], molecular dynamics (MD) [11–14], Monte Carlo [15,16], and density functional theory [17,18] methods.

It is generally agreed that it is difficult to investigate the effects of individual design variables related to nanoscale physics and the segmental motion of epoxy solely by using experiments that demand a tremendous amount of trials and errors. Moreover, limitations in the precise control of the conversion ratio, visualization of the network structure, measurement of free volume related to the aging and degradation, and inevitable measurement noise make it difficult to fully understand the designed epoxy. Therefore, the above-mentioned computer simulation techniques have also aimed at designing high-performance epoxies. In particular, MD simulations are considered to be the most effective and efficient way of probing the internal molecular structure and predicting the physical properties of thermoset polymers. Several groups have proposed specific modeling procedures to describe the real structural characteristics of bulk thermosetting polymers and

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[*] Corresponding author. Division of Multiscale Mechanical Design, School of Mechanical and Aerospace Engineering, Seoul National University, Republic of Korea.
E-mail address: mhcho@snu.ac.kr (M. Cho).

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have estimated their thermo-mechanical properties [11–14]. For instance, Kim et al. observed the effect of the crosslink density on thermo-mechanical properties such as the density, elastic modulus, and coefficient of thermal expansion with respect to different crosslinking methods from the point of view of modeling [13]. Li et al. observed the evolution of the molecular structures of two thermosetting epoxy systems with different degrees of cure; they then derived various thermo-mechanical properties, including the yield and glass transition temperature [14].

Moreover, MD simulation studies on epoxy have been a part of the constitutive modeling of composites, especially for the modeling of nanocomposites, which requires the elucidation of important nanoscale characteristics related to their interface or interphase features [19–26]. In this regard, various thermo-mechanical properties of epoxy have been predicted and used to establish constitutive models that are essential in composite micromechanics theories.

While MD simulations play an important role in identifying nano-phenomena under diverse physical situations for amorphous polymer-based materials, the extreme thermo-mechanical loading demands thorough consideration of polymer yielding in order to guarantee and further extend their engineering applications. Prior to the computational approaches in polymer design, the molecular theoretical description for the yield of amorphous polymers was developed from several points of view. Based on the Arrhenius formulation for reaction rates, Eyring first described the yielding of polymer chains as a process of viscous plastic flow induced by the transition that is thermally activated between different equilibrium states on the potential energy surface [27]. Eyring's theory contributed to the deformation kinetics of amorphous polymers, and acted as the foundation of transition state theory. Robertson [28] asserted that the conformational change in the molecules is the origin of polymer chain flow, and that the fraction of high-energy *cis* conformation is maximized through the effect of shear stress on the polymer chains, culminating in the initiation of yield. In addition to the mechanistic explanations of Eyring and Robertson, alternative models for the yielding of polymers – which rely on the concepts of dislocations and disclinations from the deformation mechanisms of conventional crystalline materials – were suggested by Bowden and Raha [29], and Argon [30,31]. More specifically, Bowden considered the origin of yield as small shear strain region, which is analogous to a dislocation loop. On the other hand, Argon noted that the creation of kinks in the polymer chain gives rise to the rearrangement of internal structures, thereby changing the potential energy of the polymer. Recently, studies on the yielding mechanisms have been extended with the aid of computational approaches that enable the direct observation of the plastic behavior of amorphous polymers at the atomic scale [4,32,33].

Although MD simulations have been effectively used in establishing the fundamental background of the elasto-plastic deformation behavior of amorphous polymers, the temporal scale problem arising from extremely short time step, which stems from the computational limitations in the time integration of the equations of motions to obtain quasi-static mechanical response of polymers, remains a challenging issue. It has been generally agreed that in both experimental [34–41] and simulation studies [4,42–44], the yielding of an amorphous polymer is a rate-dependent phenomenon because of its viscoelastic nature; thus yield stress increases with the increasing strain rate. Therefore, owing to the huge time scale gap between the experimental and computational contexts, it is inevitable that notable differences will be observed in the evolution of deformation, which results in quantitative discrepancies of the stress-strain response. The most commonly used strategy that can be used to resolve this problem is coarse-graining [44] by reducing the number of the degrees of freedoms in full-atomic MD simulations. Nonetheless, coarse-graining still requires sophisticated parameter fitting without losing geometric information concerning all atoms. Therefore, an alternative acceleration method to account for the effect of the strain rate on the yielding of polymers is required in order to reduce the gap between mechanical response predicted by simulation and realistic macroscopic behavior over multiple temporal scales.

In this study, inspired by the abovementioned requirements, we propose an efficient temperature-accelerated method for MD simulations to predict the elasto-plastic behavior of an epoxy polymer across a wide range of strain rates, including quasi-static (experimental low strain rate) conditions. By establishing a correlation between the temperature and strain rate on the basis of transition state theory, the time (strain rate)-temperature superposition method (with incorporated shift factors) is developed to predict the yield strength of epoxy at various strain rates without losing geometric information at the atomic scale. From the uniaxial tensile simulations, the stress-strain responses of crosslinked epoxy are derived at various temperatures and strain rates. In addition, changeable shift factors (corresponding to variations of temperature and strain rate) are introduced to take into account inherent nonlinear characteristics of the epoxy yielding. Together with constructed Eyring plot from suggested accelerated method, quasi-static stress-strain response is also predicted and validated with experimental results.

2. Models and methods

2.1. Theoretical model

To account for the quasi-static mechanical behavior, which is not available in classical MD simulations, we also utilize the concept of temperature-accelerated dynamics (TAD). According to Eyring's model and extended models [45,46], it is revealed that negative temperature dependency and positive strain rate dependency are directly associated with the yielding of glassy polymers. Therefore, if a proper quantitative characterization is enabled between the strain rate and yield strength, and between the temperature and yield strength, the limitation in enlarging the time scale required to consider the slow strain rate within the available Eyring plot can be overcome. The TAD model enables the acceleration of the transition from one state to other states by incorporating thermal activation energy to promote the transition. In combination with transition state theory and the concept of TAD, the inherent time scale limitation of MD simulations can be overcome by elevating the simulation temperature.

As a representative model for describing the polymer yield on the basis of transition state theory, the Ree-Eyring model [45] (modified from the Eyring equation for yield stress) was suggested as follows:

$$\frac{\sigma_y}{T} = A_\alpha \cdot \left(\ln(2C_\alpha \dot{\varepsilon}) + \frac{Q_\alpha}{kT} \right) + A_\beta \cdot \sinh^{-1}\left(C_\beta \dot{\varepsilon} \exp\left\{ \frac{Q_\beta}{kT} \right\} \right), \tag{1}$$

where σ_y, T, k, and $\dot{\varepsilon}$ are the yield stress, temperature, Boltzmann constant, and strain rate, respectively. $Q_i (i = \alpha, \beta)$ is the activation energy corresponding to the two rate processes of α and β, and A_i and C_i are activation constants. In this model, the strain rate and temperature dependencies on the yield stress are described quantitatively by the activation parameters. While Eyring's initial equation (which fails to describe the yield behavior across a broad range of temperatures and strain rates) considered one rate process to predict the yield stress, the Ree-Eyring model can accurately predict the nonlinear relationship between $\frac{\sigma_y}{T}$ and $\log \dot{\varepsilon}$. To accomplish this within a broad temperature range, the yield stress is defined in Eq. (1) by introducing the additional nonlinear strain rate-dependent process β via an arc-hyperbolic sine function.

In addition, Bauwens-Crowet et al. [40] introduced shifting factors (S_x and S_y) on the Ree-Eyring model following the linearized Arrhenius equation: